NOTE TO USERS

Effect of Processing Parameters on the Mechanical Properties of Carbon/PEKK Thermoplastic Composite Materials

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A Thesis

in

The Department

of

Mechanical and Industrial Engineering

Presented in Partial Fulfillment of the Requirements

for the

Degree of Master of Applied Science

at

Concordia University

Montreal, Quebec, Canada

April 2005

Your file Votre référence
ISBN: 0-494-04429-2
Our file Notre référence
ISBN: 0-494-04429-2

ABSTRACT

Effect of Processing Parameters on the Mechanical Properties of Carbon/PEKK Thermoplastic Composite Materials

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This work presents the effects of processing parameters on the mechanical properties of Carbon/PEKK thermoplastic composite laminates. Semi-crystalline PEKK polymer based composites are gaining interest of many researchers due to their higher glass transition temperature (156°C), high strength and stiffness, high toughness, low moisture absorption and excellent environmental resistance. The moderate processing temperature of PEKK polymer (330-380°C) has enabled its processability to be easier than PEEK. Different processing conditions are applied to fabricate flat laminates from Carbon/PEKK unitape using compression molding. Subsequently, their mechanical properties are determined. The primary properties of interest include tensile strength and tensile modulus for 0° and 90° laminates. Maximum tensile strengths for 0 and 90 degrees laminates are found to be 2130 MPa and 80 MPa respectively. Their maximum moduli are 161 GPa and 10.5 GPa respectively. The effects of the consolidation parameters on the mechanical properties are examined. Scanning Electron Microscopy is performed to observe the difference in microstructure due to the variable processing conditions. A processing window to obtain optimum properties for the laminates is established. The investigated range of parameters can serve as a guide to consolidate Carbon/PEKK laminates for high performance aerospace applications.

ACKNOWLEDGEMENTS

It is indeed a great pleasure for me to take this opportunity to acknowledge all of those without whom this work would have been impossible. First of all, I would like to express my profound indebtedness to Dr. S. V. Hoa for his continued support during the whole program. He has always been supportive, patient and encouraging. His profound knowledge and thoughtful instructions have always shed some light on my way to pursue this work.

I would like to thank CRIAQ for commencing the project. I wish to extend my gratitude to Bell Helicopter Textron Canada Limited for their active participation in the project. Special thanks to CYTEC, USA for supplying the material for the project. I'm grateful to Dr. Johanne Denault of Industrial Materials Institute (IMI) of NRC for allowing use of the DSC facilities.

I wish to thank many of my friends and colleagues for providing a stimulating environment and extending their technical expertise whenever necessary. In particular, David Leach (CYTEC), Ali Yousefpour (AMTC), Dave Gahunia (BHTCL), John Elliot (Concordia University) and Dr. Ming Xie (CONCOM) for their technical expertise. I'm indebted to Louis Laberge Lebel, Fredrick Guay and Khassan Mourtazov for being my best friends and morally supportive. I appreciate their contribution to assist in many intricate situations during the research work.

Finally, and most prominently, I wish to express gratitude to my family, especially to my parents, Rashed Ali and Hasina Begum, for not putting any frontier to my aspirations. They have always been enduring, encouraging and caring to my priorities. I thank them for inspiring me to accomplish this work. To them, I dedicate this thesis.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 Composite Materials

Composites differ from traditional materials in that composite parts comprise two or more distinctly different components – fibers and a matrix material (most often a polymer resin) – that, when combined, remain discrete but function interactively to make a new material whose properties cannot be predicted by simply summing the properties of its components. In fact, one of the major advantages of the fiber/resin combination is its complimentary nature. By contrast, many polymer resins are weak in tensile strength but are considerably tough and malleable. When combined the fiber and resin each counteract the other's weakness, producing a material far more useful than either of its individual components.

High strength and light weight remain the winning combination that propels composite materials into new arenas, but other properties are gaining recognition as well. Composite materials offer good vibrational damping and low co-efficient of thermal expansion, characteristics that can be engineered for specialized applications. Composites are resistant to fatigue and provide design and fabrication flexibility that can significantly decrease the number of parts needed for specific applications – which translates into a finished product that requires less raw material, fewer joints and fasteners and shorter assembly time. Composites have proven resistance to temperature extremes, corrosion

and wear, especially in industrial settings, where these properties do much to reduce product life-cycle costs.

1.2 Thermoplastics and Thermosets

The advanced polymer composite application is dominated by composites processed with thermoset matrix resins. These composites have already found widespread applications in the aircraft, aerospace, defense, automotive, marine and sports communities. In the last few decades, considerable advancement has been made in perfecting the thermoset based composites. In spite of this progress, certain deficiencies remain including limited shelf life, insufficient toughness, low strain to failure, long and rigid multi-step processing and moisture sensitivity. Thermosets are generally liquid resins which are cured to achieve a crosslinked molecular structure. The cross linking reactions lead to the formation of an insoluble or infusible rigid product, in which chains of polymers are joined together to form a three-dimensional structure [1, 2].

In contrast to crosslinking thermosets, whose cure reaction cannot be reversed, thermoplastics undergo physical changes and harden when cooled but retain their plasticity, that is, they will soften and can be reshaped again and again if heated above their processing temperature. In early 1980's, the composite industry began evaluating a new generation of composites utilizing thermoplastic matrix polymers. These newer thermoplastic composites are based on aromatic polymers. In general, these less expensive thermoplastics have an indefinite shelf life, low moisture absorption, excellent thermal stability, high toughness and damage tolerance, short and simple processing cycles and potential for significant reductions in manufacturing costs. In addition, they

have the ability to be remelted and reprocessed and also damaged structures can be repaired by the application of heat and pressure.

Thermoplastic polymers are not new; they have been known for a long time. It is only recently that the newer so-called high temperature and high performance thermoplastics have been introduced [3].

Because of their advantages over thermoset composites, researchers are focusing their interests towards this high performance category of thermoplastic composites to explore the feasibility of their utilization to applications like aerospace industry. Among many of the existing high performance thermoplastic resins – Polyetheretherketone (PEEK), Polyetherketoneketone (PEKK), Polyphenylene sulphide (PPS) and Polyetherimide (PEI) – function well in high temperature environments and neither absorb nor degrade when exposed to moisture. Reinforced with high performance fibers, such as Carbon, these resins exhibit exceptional impact resistance and vibrational damping, although they present some processing challenges because of their high viscosity [4]. These processing challenges must be carefully handled and optimized to obtain good mechanical properties.

1.3 General Characteristics of Commonly Used Advanced Thermoplastic Composites

The early thermoplastic polymers had predominantly aliphatic carbon backbones in which flexible carbon chains could be extended and rotated into many configurations with relative ease. Rigidity was obtained by restricting the movement of the backbone

chain either by crystallinity or by the introduction of side groups. The major limitations with these early thermoplastics were their low elastic modulus, low glass transition temperature and poor solvent resistance. Later, a range of thermoplastics based on aromatic polymers have been developed which surmount these limitations. The introduction of rigid aromatic rings instead of aliphatic chains increases the intermolecular forces, thus restricting the movement of the backbone chain [5,6]. Hence, mechanical properties, high temperature capability and solvent resistance are greatly improved and can be often equivalent or even better than the best thermosets [3]. Melt viscosity, a polymer physical property, is much higher in high molecular weight thermoplastics than most thermosets. At processing temperature, thermosets have viscosities less than 1000 poise [7], which is much less than the viscosities of thermoplastics (Table 1.1). The low viscosity of thermosets result in high melt flow properties in the uncured state leading to good wetting of the fibers during prepreg manufacture. It was found that the desired high T_g for high temperature applications leads to high melt viscosity [8]. Unfortunately, the high melt viscosity of thermoplastics renders processing difficulty as high processing temperatures are required to achieve a low melt viscosity for good consolidation and fiber impregnation; and the viscosity may still be too high for complete impregnation of continuous fiber bundles. Processing becomes difficult at melt viscosities above 5500 poise [8]. Melt viscosities of 10^2 to 10^4 poise are desirable for the fabrication of composites [3]. It is then a question of compromise between processability of thermoplastic composites and their high temperature performance as reflected by T_g.

Table 1.1: Density and Viscosity of High performance Thermoplastic Resins [3].

	Victrex PEEK	PEKK	Ryton PPS
Density, g/cm^3	1.30	1.30	1.36
Viscosity (poise) @ processing temperature	34000	25000	25000

Among many other parameters, the performance of thermoplastic composites in high temperature environments depends on thermal properties like T_g of the polymer matrix, and its morphology [9]. Below T_g, a polymer, either amorphous or semi-crystalline, is in a glassy state while above T_g, the material softens as the temperature increases and the material becomes rubbery.

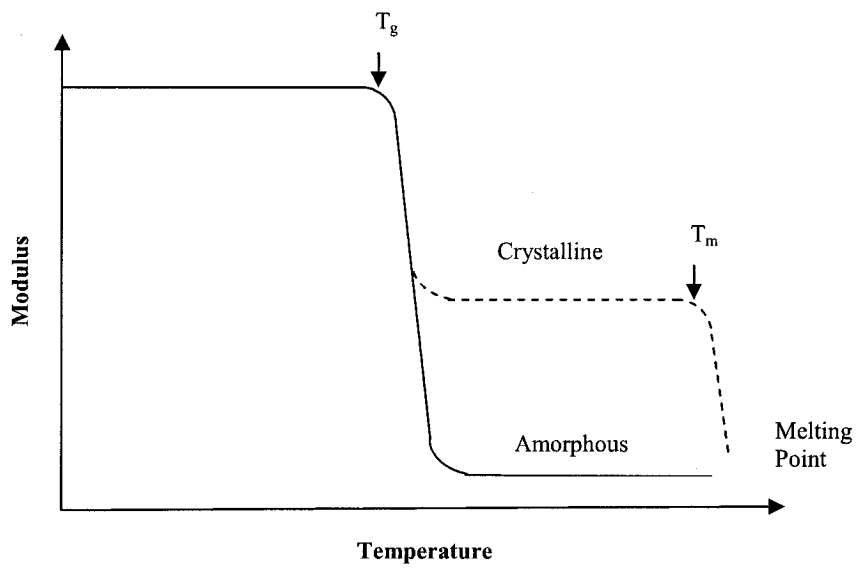


Figure 1.1: Semi-Crystalline thermoplastic polymers retain part of their properties above T_g

As shown in figure 1.1, when heating a semi-crystalline polymer above T_g, the amorphous regions of the polymer can flow plastically and therefore heating is accompanied by a reduction in the polymer stiffness which may occur over a broader

range of temperatures. A 100% crystalline polymer would eliminate the glass transition process and replace it with the melting process, but the excessive crystallization would impair the ductility of the resin [3]. At temperatures between T_g and T_m the semi-crystalline polymer consists of rigid crystalline regions dispersed in a soft amorphous matrix, so that the polymer is flexible. The properties of the semi-crystalline thermoplastics are then significantly reduced, but to a lesser extent than in amorphous thermoplastics; they retain a portion of their load-bearing properties, but not above the melting temperature, T_m. Amorphous thermoplastics do not have a true melting temperature as melting is the disassociation of the crystalline structure [10], but they go through a glass transition. Above T_g, amorphous thermoplastics exhibit substantial loss of their mechanical properties. Leach et al. [9] showed that the long term service temperature of the composite is 25-30° C below the T_g of the matrix; hence continuous use service temperature for the thermoplastics could be lower.

Mechanical properties like high resin strength values are desirable to minimize intra-ply cracking in the composite under impact conditions and to obtain good transverse properties [3].

Table 1.2: Tensile and flexural properties of high performance thermoplastic resins [3].

	Tensile Strength (MPa)	**Tensile Modulus (GPa)**	**Elongation at break (%)**	**Flexural Strength (MPa)**	**Flexural Modulus (GPa)**
Victrex PEEK	100	3.1	40	110	3.9
PEKK	102	4.5	4		
Ryton PPS	82.8	4.3	3-5	96	3.8

Tensile and flexural properties of thermoplastics are listed in table 1.2. They are often comparable and better than those of thermosets like epoxy and bismaleimide modified epoxy [3]. A major requirement in the design of aircraft for high temperature performance is the use of a resin that retains adequate stiffness at the required temperature and in a wet environment.

It is well recognized that polymers in a chemical environment can absorb, react chemically, become plasticized, dissolve and be stress-cracked. The chemical resistance of a polymer depends primarily on its chemical structure. For example, high molecular weight, chain branching, cross-linking and high degree of crystallinity increase the chemical resistance of polymers [11]. High performance thermoplastics are generally characterized by good heat and chemical resistance, better than the first generation of thermoplastics [3]. In general, semi-crystalline polymers are more solvent resistant than amorphous polymers due to the densely packed spherulites in the crystalline region which impedes diffusion of solvents into the polymer [10]. In aircraft applications, structural composite parts must be resistant to the various fluids encountered in flight and maintenance operations such as fuel, fuel additives, deicing fluids, lubricants, paint strippers and hydraulic fluids. The solvent resistance of the thermoplastics may be improved by inducing limited cross-linking into the polymer backbone through the use of annealing, postcures, or thermal reactions of terminal and pendant reactive groups [3], but these techniques often reduce fracture toughness. Studies have been conducted to investigate the aircraft fluid and chemical solvent resistance of carbon fiber reinforced PEEK and PPS composites. Tensile and flexural strength, thermal behavior and dynamic mechanical properties of composites were presented and the degradation of mechanical

properties under a paint stripper application was explored. Furthermore, crystallization enhancement of the low crystallinity composites in the presence of solvents and aircraft fluids was observed as well [12].

Maximum moisture content absorbed by thermoplastics when immersed in water is generally lower for semi-crystalline thermoplastics than for amorphous thermoplastics. Wang and Springer [13] have conducted tests to determine the moisture absorption characteristics of PEEK 150P and APC-2 composite when exposed to humid air of different relative humidities and temperatures. Wang and Springer evaluated the effects of moisture content and crystallinity on fracture toughness.

The morphology of polymers, as defined in the Encyclopedia of Polymer Science and Engineering, is concerned with the shape, arrangement and function of crystals alone or embedded in the solid. Polymers are either homogeneous amorphous or heterogeneous semi-crystalline. Amorphous thermoplastics do not contain crystalline structures while semi-crystalline thermoplastics are characterized by the presence of ordered crystalline regions as well as amorphous regions. The term crystalline polymer always implies partially crystalline. The degree of crystallinity may be as high as 60-65% in some cases [10].

Significant work has been done in studying morphology-processing and morphology-property relationships with PEEK and PPS matrices and their composites. The influence of morphology on the properties of composites is a major issue with semi-crystalline thermoplastic based composites. Factors including copolymer(s), molecular weight, presence of other materials (nucleating agents, impurities etc.) and processing conditions (melt temperature, holding time at this temperature, cooling rate etc.) can influence the

morphology [14]. Degree of crystallinity as a function of cooling rate was obtained by Talbott et al [15] and Velisaris and Seferis [16]. Kim et al [17] studied the effect of cooling rate on the residual stress in a thermoplastic composite. The effect of crystallinity on the mechanical properties of PEEK has been explored by Talbott et al. [15]. Xiao and Hoa [18] showed that crystallinity of PEEK is also influenced by the temperature to which the polymer is heated and the time it is held there. These authors mentioned that high melt temperature leads to lower crystallinity. This might be of a great concern during a repair process using welding techniques. They also mentioned, heating is localized at the damage area while the surrounding areas are subjected to lower melting temperatures resulting in undesired changes in degree of crystallinity and then mechanical properties in those surrounding areas.

Talbot et al. [15] presented toughness and tensile strength properties of neat PEEK resin as a function of degree of crystallinity. In general, a lower level of crystallinity will produce higher elongation and better toughness but with the trade-off of lower strength, thermal stability and chemical resistance.

The processing science of thermoplastic composites is also a considerable challenge for the researchers to develop composite parts with optimum properties. Speaking of the benefits of thermoplastic composites, in addition to their unlimited shelf life and short processing times, thermoplastic composites have the ability to be remelted and reprocessed. But at the same time the major challenges to be considered are high melt viscosity and high processing temperatures [3, 46, 48]. This issue is discussed in detail in chapter 2 of this thesis. Flow behavior of thermoplastic composites [46, 48, 51, 54, 56] is also discussed in the subsequent chapter.

There is considerable interest in advanced thermoplastic composites for high performance applications which is evident from the ongoing and increasing interest in research and development of thermoplastic composites. The difficulty in processing because of high melt viscosity of thermoplastics draws attention to the researchers to obtain higher elevated temperature performance. At the same time, effects of crystallinity (morphology) on the mechanical properties were also investigated as a foremost issue. Since higher processing temperatures are involved in thermoplastic composite manufacturing, the residual stresses are important concerns in predicting the final properties of the laminates. The interfacial adhesion between fiber and matrix is also a key point that has been considered by the researchers. Thermoplastic composites exhibit good fatigue and creep behavior in general. Besides PEEK and PPS, whose database is quite extensive, the mechanical behavior of other thermoplastic composites needs to be investigated.

1.4 Previous Works done on Advanced Thermoplastic Composites

High performance fiber reinforced thermoplastics have already made their way in all possible sectors of composite applications side by side with thermoset based composites. Significant work has been done on physical, chemical and thermal properties of thermoplastic neat resins as well as processing, microstructural, thermal and mechanical properties of their composites based on Carbon, Glass or Aramid or any other high performance reinforcements.

A comparing scenario of different high performance thermoplastic matrices is presented in Table 1.3.

Table 1.3: High Performance Polymer Thermoplastic Matrices [19].

		PEI	PPS	PEEK	PEKK
Morphology		Amorphous	Semi-Crystalline	Semi-Crystalline	Semi-Crystalline
T_g, (°C)		217	90	143	156
Typical Process Temperature (°C)		330	325	390	340
Comments	Pros	- High T_g - Moderate Processing Temperature	- Excellent Environmental Resistance - Moderate Processing Temperature	- Extensive Database - Excellent Environmental Resistance - High Toughness	-Excellent Environmental Resistance - High Toughness - Lower Process Temperature than PEEK - Bonding and Painting
	Cons	Environmental Resistance	- Low T_g - Low Toughness - Low Paint Adhesion	- High Process Temperature - High Polymer Cost	- Limited Database in Composite form

Among many other high performance thermoplastic polymers like PEEK, PPS and PEI, semi-crystalline PEKK is one of the potential polymers that can be used for structural applications because of its excellent environmental resistance and higher toughness. PEKK has lower processing temperature than PEEK and higher mechanical properties than PPS and PEI, which makes PEKK a prospective candidate for use in fiber reinforced high performance applications [19].

However, the only shortcoming is the limited database of the material. In contrast to PEKK, PEEK has an extensive database in terms of material processing and performance

and been successfully used in numerous applications. Cogswell et al. [20, 21], Leach et al. [22-25] and Denault et al. [26-29] have obtained significant results on the processing, morphology, delamination behavior and mechanical performances such as tensile and fatigue strength of Carbon/PEEK composites. A group of researchers in Kyoto Institute of Technology, Japan have developed an innovative micro-braided fiber reinforced thermoplastic yarn. Their primary interest was focused mostly on PA6, PA66, PPS, PEI, PP, PEI and PET based composites in the form of braided yarns and knitted fabrics. The investigations were directed more on exploring the processing, impregnation quality and effects of those on the mechanical properties such as tensile, compressive, damping and flexural strengths [30-35]. Lebel et al. [36] also studied mechanical properties of Carbon/Nylon6 braided laminates along with Micro braided tows and interpreted the properties in terms of impregnation quality dependant on the processing parameters. Bigg et al. [37] determined strength and modulus for PET, PP and PEK based composites reinforced with continuous and long discontinuous fibers.

Chang and Benjamin [38] investigated the thermal properties of PEKK matrix and its composites while characterizing the material. Crystallinity, melt rheometry, pressure-volume-temperature relations, thermal expansion, thermal conductivity and heat capacity are a few of the properties those were measured in their work.

The processing and crystallization behavior of PEKK matrix was observed by Ferrara and Seferis [39] using the Velisaris-Seferis crystallization kinetics model developed for PEEK. Tzeng [40] predicted a model and experimentally verified the residual stresses in PEKK based composite parts. Bucher and Hinkley [41] performed experiments with AS4/PEKK composites which showed excellent correlation between resin/fiber contact

angle and composite transverse flexural strength as measures of resin/fiber interfacial strength. They also discussed the fiber effects on interlaminar fracture and on the in-situ crystallization of the matrix during composite fabrication.

It is apparent from the literature that there remains a scarcity of investigation on the mechanical performance of PEKK based composites. Although in the late 80's a few researchers explored some of the mechanical performances of fiber reinforced PEKK composites. Pratte et al. [42] presented a mechanical performance comparison between Long Discontinuous Fiber (LDF) Carbon/PEKK composites with continuous carbon fiber reinforced PEKK composites. At the fundamental mechanical or micromechanics level, fibers in LDF materials have the unique ability to slide by each other to accommodate thermoforming of complex shapes. This is achieved uniformly within a specific oriented tape ply on a random individual fiber basis in response to the associated stress field developed during shaping. LDF technology coupled with high performance PEKK, offers high potential pay offs for new, lower cost design and manufacture. Pratte manufactured semi crystalline PEKK based laminates by consolidating a multi-ply sequence of unidirectional tape prepreg in either a preheated press or an autoclave. For press molding, the consolidation parameters were: temperature 360 – 370°C, dwell time 5-15 minutes and pressure about 2.0 MPa. For the autoclave cycle, the parameters consisted of a temperature ramp to 370°C under 300 KPa pressure, followed by increase to 2.0 MPa pressure with a dwell time of 30-60 minutes for consolidation and then cooled at a rate of 3-4°C/min. Table 1.4 summarizes the investigation results [42] of mechanical property levels of unidirectional LDF carbon fiber/PEKK composites at room temperature.

Table 1.4: Room Temperature unidirectional mechanical properties of Carbon fiber AS-4/PEKK laminates [42].

Property	Units	LDF System	Continuous Fiber System
Tensile			
Strength (0°)	MPa	1613	1675
Modulus (0°)	GPa	123.4	129.6
Poisson Ratio			
Strength (90°)	MPa	91	73
Modulus (90°)	GPa	10.3	8.3
Compressive			
Strength (0°)	MPa	1262	1393
Modulus (0°)	GPa	110.2	121.4
Flexural			
Strength (0°)	MPa	1655	1930
Modulus (0°)	GPa	124.1	127.5
Shear			
Inplane Strength	MPa	146	142
Inplane Modulus	GPa	5.5	5.5
Short Beam Shear	MPa	110	117

Properties like interlaminar delamination characteristics and edge delamination test behavior were presented. Damage tolerance behavior was evaluated by open hole tension, open hole compression and compression after impact tests. Pratte also investigated the environmental durability by assessing effect of moisture and solvent exposure on the laminates. The investigation verified that preliminary design allowable characterization of LDF carbon/PEKK thermoformable laminate sheets shows high structural design potential toward efficient component performance.

Chang [43, 44] presented a comparison of PEKK and PEEK neat resin properties like density, melting point, glass transition temperature, processing temperature, tensile

strength, tensile modulus, % elongation, limiting oxygen index etc. Table 1.5 has the summary of the comparison.

Table 1.5: Properties of PEKK and PEEK neat resins [43, 44]

Property	Units	PEKK	PEEK
Density	g/cc	1.3	1.3
Melting point	°C	338	340
Glass transition temp.	°C	156	144
Processing temp.	°C	360-380	370-380
Tensile strength	MPa	102	103
Tensile Modulus	GPa	4.5	3.8
Break Elongation	%	4	11
Limiting oxygen index	%	40	35

Chang [43, 44] made carbon/PEKK laminates from melt impregnated precursor tows (used for unidirectional laminate manufacturing), tapes and fabrics (used to manufacture quasi-isotropic 0,90,±45 laminates) using a compression molding technique. These laminates were tested for flexural strength, short beam shear strength, hot-wet compression strength, compression after impact and finally the results were presented. Mechanical properties of AS-4/PEKK laminates obtained by Chang are presented in table 1.6.

Table 1.6: Mechanical properties of AS-4/PEKK laminates [43,44].

Property	Temperature, °C	Value
Flexural strength, MPa	23	1620
	93	1394
	93, wet	1379
Short beam shear strength, MPa	23	117
	93	97
	93, wet	92
Compressive strength, MPa	23	1393
	82, wet	1234
Compression after impact		
Compressive stress, MPa	23	274
Compressive strain, %	23	0.6

Chang concluded that similar to other aromatic polyetherketone resins, PEKK showed excellent environmental resistance, low moisture absorption, good flammability characteristics and high thermal/hot-wet stability as required for aerospace applications in advanced composites. Chang's investigation also established that in comparison to AS-4/3501 epoxy, AS-4/PEKK composites have excellent hot-wet stability, environmental durability, interlaminar fracture toughness and good damage tolerance performance.

In another literature, Chang [45] presented the updated overview of the thermoplastic matrix composites technology which has been developed and upgraded during 1988-1991. Chang summarized some mechanical property results of PEKK based composites obtained from previous work [42] (mentioned in table 1.4) and showed a comparison of mechanical properties of KEVLAR®/PEKK and KEVLAR®/ EPOXY based composites. Table 1.7 lists the mechanical properties of KEVLAR®/PEKK and KEVLAR®/EPOXY.

Table 1.7: Mechanical properties of KEVLAR®/PEKK vs. KEVLAR®/EPOXY [45].

Property	KEVLAR®/PEKK	KEVLAR®/EPOXY
Tensile modulus (0°)	76 GPa	55-70 GPa
Tensile strength (0°)	1240 MPa	1100-1400 MPa
Flexural Modulus (0°)	64 GPa	70-80 GPa
Flexural strength (0°)	760 MPa	550-700 MPa
Short beam shear (0°)	55 MPa	30-60 MPa
Tensile modulus (0°)	6 GPa	3-7 GPa
Tensile strength (0°)	18 MPa	10-20 MPa

Chang discussed different thermoplastic systems available in the market, LDF composites technology for cost-reduced manufacturing, comparison of mechanical properties (fatigue and creep) between LDF system and continuous fiber and the applications of these composites in various aircraft parts. Chang concluded that the LDF system is equivalent to the continuous fiber counter part in static or dynamic mechanical properties and no adverse effect of discontinuous fiber ends has been observed in the property performance. The technology was demonstrated via "parts" manufacturing such as V-22 tiltrotor aircraft wing ribs and rotorcraft curved light frames by stretch forming.

CYTEC Engineered Materials, a manufacturer of polymers and composites, based in California, USA, had also performed some of the mechanical property evaluations on Carbon/PEKK and Glass/PEKK laminates made from unidirectional prepreg tape using autoclave technology. CYTEC gave 315±10°C as the temperature, 200±100 psi (1.38±0.68 MPa) as the pressure and 10±5 minutes as the time during the consolidation

cycle of the laminate manufacturing. The results obtained from the composite laminates are listed in table 1.8.

Table 1.8: Unidirectional Cabon/PEKK and Glass/PEKK laminate properties [19].

Property	Units	PEKK/ AS4 Carbon	PEKK/ S-2 Glass
0° Tension: ASTM D3039			
Modulus	GPa	133	51.8
Strength	MPa	2050	1675
Poisson's ratio	-	0.30	0.27
0° Compression: SACMA SRM-1			
Modulus	GPa	124	20.1
Strength	MPa	1350	1213
90 Tension: ASTM D3039			
Modulus	GPa	9.47	20.1
Strength	MPa	56	48
In-Plane Shear: ASTM D3518			
Modulus	GPa	5.56	7.0
Strength	MPa	131	108
Short-Beam Shear: ASTM D2344			
Strength	MPa	98	74

The work of the researchers mentioned above [19, 42-45] was mainly on the exploration of neat PEKK resin properties and the mechanical performance evaluation of PEKK based composites to verify its usability in high performance applications. Property evaluation of PEKK based composites found in the literature proves their strong existence in the regime of advanced thermoplastic composites. However, as mentioned by these researchers, the final properties of these composites are strongly dependent on the processing parameters. The comprehension of the connection between the processing parameters with the final laminate properties has not been investigated by any of the researchers who worked with PEKK based composites. There is a necessity that the existing boundary of the research work on PEKK based composites should be extended

towards the understanding of the effects of processing parameters on the final properties of the laminates. This extension will enhance the knowledge of characterization of the material in terms of processing window and can be significantly supportive to the ongoing research and development on PEKK based composite applications.

1.5 Rationale for Work on Carbon/PEKK Composite

The ongoing demand of composites to high performance applications entails more research and development on both existing and new materials and their feasibility of utilization in all possible ways. There exist many examples where composites are replacing metallic parts and gaining reliance because of their advantages. The inertia in utilizing high performance thermoplastic composites in structural applications is attributed mainly to the unanswered questions concerning their poor compression properties, fatigue and creep behavior, lack of processing experience, the high cost and the limited data base. This comment is more meaningful for other thermoplastics like PEKK that deserve attention besides PEEK and PPS.

Keeping in mind the turnovers of composite structures, Bell Helicopter Textron Canada Limited pursued an interest in replacing the existing Aluminum helicopter landing gear with composites, especially thermoplastic based composites. The priority to thermoplastic based composites undoubtedly lies in their superior toughness, over their peers, which is one of the major requirements of the application. The absorption of high amount of energy by the landing gears is a crucial necessity when the helicopters lands on them. The other pre-requisites for the application are - high temperature capability, excellent environmental resistance and cost effectiveness.

To opt for a material that is suitable for such an investigation, PEKK based composites conforms to the stipulation of the application. PEKK is cheaper than PEEK, a cut above in mechanical properties when compared to PPS and PEI, lower processing temperature than PEEK which facilitates better handing of material during fabrication and higher glass transition temperature, T_g [19]. Hence PEKK based composite properties need to be investigated in depth in terms of variable processing conditions. This will facilitate the understanding of the material performance under different manufacturing conditions. The lack of data base calls for a study on processing of PEKK based composite laminates and their effects on mechanical properties. Thus a better understanding on the flow behavior and processing parameters is essential to obtain optimum properties for PEKK based composite components. Since the variation in processing parameters affects the morphology of the resin content and eventually the mechanical properties, a study on comprehending the connection between the processing parameters, morphology and mechanical performance is indispensable.

1.5 Objective of the Thesis

The primary objectives of the thesis are:

1. To investigate the significance of processing parameters on consolidating fiber reinforced PEKK based laminates and to evaluate the influence of these parameters on the mechanical properties of the laminates.
2. To comprehend the connection between processing parameters, consolidation quality and mechanical properties and use the results to achieve optimized processing conditions.

3. To obtain an optimum processing window to manufacture PEKK based fiber reinforced laminates which will eventually be applicable for high performance applications.

1.6 Organization of the Thesis

The present chapter gives an overview about composite materials, thermoset and thermoplastic resins, general characteristics of the thermoplastic composites, a description of previous work that has been done on advanced thermoplastic composites, the rationale for the work of the thesis and finally the objective of the thesis work. The review of previous work covers brief coverage on a few of the high performance thermoplastic based composites and a detailed survey on the processing and mechanical properties of PEKK based composites.

Chapter 2 describes the processing science and flow process in thermoplastic composite laminates. It also contains the importance and function of the processing parameters.

Chapter 3 includes the information on material that is used for this work. In addition, the manufacturing methods of laminates, thermal analysis, microstructural observations and mechanical testing procedures are also presented.

Chapter 4 combines all the test results and discussions obtained from the laminates. The chapter also highlights the link between all the different steps towards obtaining a range of optimum results.

The thesis culminates with chapter 5, imparting the conclusion and contribution of present thesis work and recommendations for future work.

CHAPTER 2

PROCESSING SCIENCE OF THERMOPLASTIC COMPOSITE MATERIALS

2.1 Introduction

This chapter presents the processing techniques of continuous fiber reinforced composites with thermoplastic matrices. These composites are considered advanced materials because high performance properties can be achieved by incorporating high fiber volume fractions and by controlling fiber alignment. The benefits and disadvantages of processing thermoplastic composites compared to thermoset composites are discussed. This chapter also focuses on the flow behavior of continuous fiber reinforced thermoplastic composites.

2.2 The necessity of understanding the processing science of thermoplastic composites

Structural composites are a rapidly growing family of materials including systems of high levels of continuous fiber reinforcement, in particular of carbon fiber, embedded in a matrix resin. The key property of such materials is their high stiffness and strength per unit weight, making them particularly attractive systems for aerospace structures and

sporting goods where the anisotropic nature of the materials can be exploited to achieve novel design strategies.

Today, this family of materials is largely based on the impregnation of the reinforcing fibers by low viscosity monomers followed by a labor intensive, and protracted, manufacturing cycle involving the polymerization of the resin in situ, usually by a thermosetting crosslinking reaction. The very rapid growth in the use of such materials, presumes an improvement in product quality in certain areas such as damage tolerance and the resistance to hostile environments; and predicts the development of efficient mass production technology so that the experience of industries such as aerospace and sporting goods can be transferred into the general area of industrial products [46]. Both the presumption of improved product performance and the prediction of mass production technology may be realized in the translation of advanced composite materials from crosslinked, thermoset resin system to linear chain, thermoplastic polymers [47]. The characteristic of thermoplastic material is that it can be processed by a simple physical process of heating and shaping. By removing chemistry from the fabrication stage it allows the processor to concentrate resources and skills on the primary art of making shapes; then, thermoplastics offer new opportunities for mass production technologies. Finally, the provision of a tough, environmentally resistant, resin provides enhanced tolerance of harsh service conditions [47].

Thus, with thermoplastic composites, there lies a promise of combining enhanced service performance with high rate of manufacturing technology. To fulfill that promise there is an urgent need to understand the processing science for such materials.

2.3 Advantages and Disadvantages of processing thermoplastic composites

The primary benefits in processing thermoplastic composites compared to thermoset composites are the unlimited shelf life, the short processing time and their ability to be remelted and reprocessed. These advantages make them particularly attractive from an economic point of view. For most thermoplastic composites, the shelf life is unlimited and the processing time is in terms of minutes rather than hours as it is for thermoset composites because polymerization has been completed before the combination of fibers with matrix [48]. No time is required for this chemical reaction to occur during processing as in the case of a thermoset. Thermoplastics have also the ability to be processed at various heating and cooling rates due to the absence of the exotherm experienced in the case of thermosets. This may be an important issue in field repair considering the extremes encountered in processing conditions. However, control of cooling rate in the case of semi-crystalline thermoplastics is very important in determining the morphological structure and mechanical properties of the final composite.

The capability of thermoplastics to be remelted has led to the development of novel manufacturing technologies. Thermoplastic laminates showing voids or defects can be reconsolidated to eliminate these defects whereas a thermoset would be rejected. Excess or scrap material may be reused. Complex three dimensional parts can be shaped or formed from a flat consolidated sheet. Composite parts can be thermally joined to form a composite assembly which eliminates the need for adhesive bonds and mechanical fasteners.

The main drawbacks with processing advanced thermoplastics compared to processing thermosets are their high melt viscosity and high processing temperatures needed to melt them. The high T_g desired for advanced thermoplastic composites leads to high melt viscosity and high processing temperatures, often close to the decomposition temperatures. At such high temperatures, depending on the thermal stability of the polymer which may vary significantly from one polymer to an other, thermal and oxidative degradation and hydrolysis may occur [48]. In general, most organic linkages in high performance thermoplastic polymers become thermally unstable about 450°C [49]. The lack of tack and drape of most thermoplastic prepregs is another drawback. It is difficult to lay up prepreg plies against a contoured shape. To overcome the problems of high melt viscosity and the lack of tack and drape of prepegs, some innovative processes of combining fibers and thermoplastic polymers and producing high quality laminates have been developed in recent years.

2.4 Key aspects related to processing of thermoplastic composites

2.4.1 Quality assurance

The first ingredient of processing science is the assurance that the product which is made is indeed the product which has been sought to be made. This is important because of the fact that any change in the product during processing could change the performance of the component in service. There are two primary features of quality assurance which impact on the service performance: the molecular weight of the polymer, which controls

the toughness; and the level of crystallinity, which determines the environmental resistance [46].

2.4.2 Thermophysical properties

As a thermoplastic material, heat exchange plays a crucial role in the process economics. While heat content of the composite is typical of that of thermoplastic molding compounds at the very high processing temperatures, the very high loading of fibers greatly enhances heat transfer. Despite the high enthalpy of the system resulting from high processing temperatures, the presence of the reinforcing fiber gives rapid, and anisotropic, heat transfer. In practice the principle constraint on rapid fabrication will not be heat transfer within the material itself but rather the efficiency of heat exchange at the surface of the material and the thermal inertia of the surroundings. An important result of this combination of good heat transfer within the material but relatively poor heat transfer at the surface is that temperature gradients and, in particular, cooling rate gradients, are relatively shallow throughout the molding [50].

In any heat exchange process there will be dimensional change. In carbon fiber composites axial expansion is constrained by the very low thermal expansion coefficient of the fiber. Table 2.1 indicates that across the fiber direction the thermal expansion is more closely related to that of the resin [46].

Table 2.1: Linear thermal expansion of fiber [46].

	23 to 143 °C (per °C)	143 to 343 °C (per °C)
Along fiber 0°C	0.5×10^{-6}	1×10^{-6}
Across fiber 90°C	30×10^{-6}	75×10^{-6}
Quasi isotropic $(-45°, 90°, 45°, 0°)_s$	2.9×10^{-6}	-

The anisotropy of thermal expansion must be taken into account when laying up a molding: a proper symmetry must be maintained particularly when molding large area flat panels [50].

2.4.3 Strategies for molding shapes

There are two distinct approaches to making shapes from thermoplastic composite materials: a) preimpregnate the fibers with the resin and then mold into shape; b) arrange the reinforcement and resin together in the mold and then consolidate and impregnate simultaneously. Different product forms and impregnation strategies are shown in figures 2.1 and 2.2.

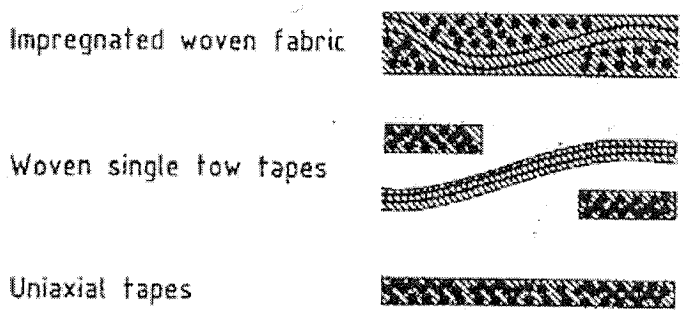
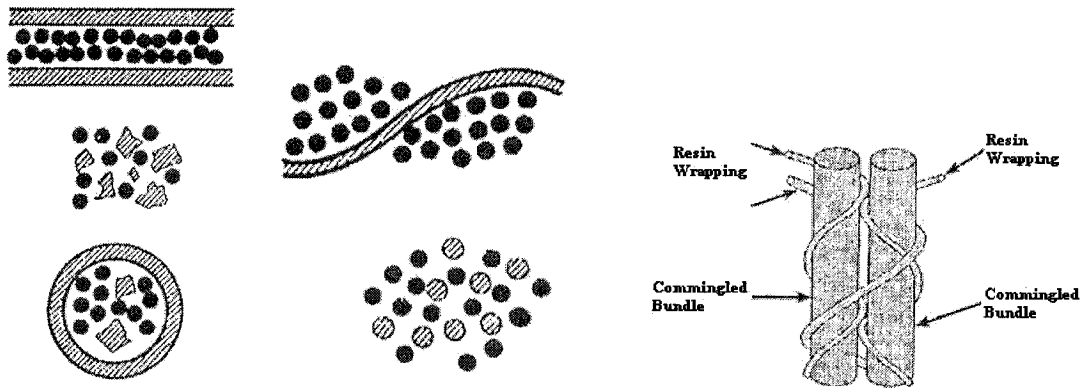


Figure 2.1: Preimpregnated product forms



(a) (b) (c)

Figure 2.2: Post shaping impregnation strategies: (a) Film stacking, Powder coating, Powder coating plus skin, (b) Co weaving, Hybridisation and (c) Commingled yarn.

The principle advantage of impregnation after shaping approach, especially for drapeable products such as co-woven or hybridized fiber, is the potential for forming a complex shape by hand and subsequently consolidating. The most evident disadvantage of this approach is that it requires a relatively protracted molding cycle in order to carry out the impregnation stage and that impregnation stage contributes to product quality in two different ways. One is by defining the microstructure of the molding and the other one is by establishing the interface between the resin and the fiber on which the service properties of the composite depend [46].

Preimpregnated product forms have their own particular advantages. Impregnated woven fabrics are most appropriate for thin skinned structures; woven single tow tapes including tied uniaxial materials, offer modest drapeablity and can be made as very broad products; uniaxial tapes are the most versatile product especially suitable for designing anisotropic components.

2.5 Consolidation of thermoplastic composite

Consolidation is the process step used to obtain a void free composite part through the bonding of prepreg plies (tape prepreg) or complete impregnation (commingled tow). During consolidation, an external pressure is applied to a composite part. This pressure attempts to squeeze out entrapped air, suppress voids and uniformly disperse the fibers. Processing and material parameters play a key role in determining the optimum process for consolidation [48].

To produce a fiber reinforced thermoplastic composite, the prepregs have to go through three major steps [3,48].

1. Melting
2. Consolidation
3. Solidification

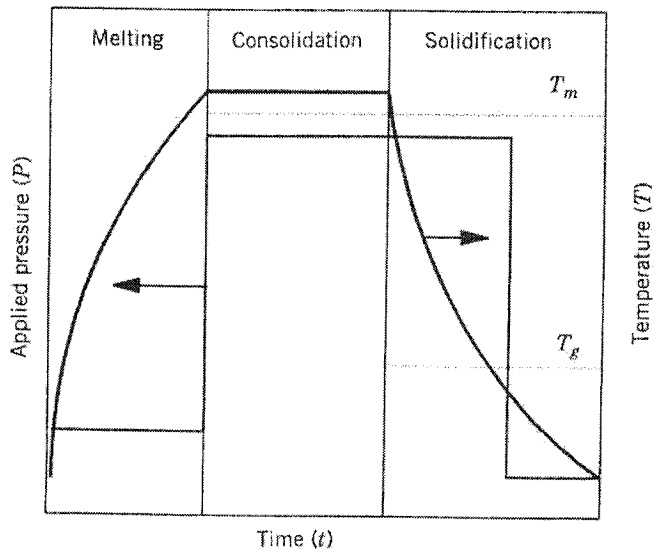


Figure 2.3: PTT profile for a typical thermoplastic composite processing [48].

2.5.1 Melting

Before consolidation, thermoplastic composites must be heated in order to melt the matrix resin and bond the surfaces. During heating, a low pressure can be applied. If the composite does not contain solvents and volatiles in its matrix, then rapid heating is preferred for short processing cycles (filament winding, tape layup, pultrusion) [48]. In crystalline structures, the peak processing temperature is preferred to be higher than the melting temperature in order to erase all spherulite nuclei and then produce a new more uniform crystalline morphology [3].

2.5.2 Consolidation

Once the matrix is molten, a consolidation pressure is applied resulting in decrease in thickness of the composite.

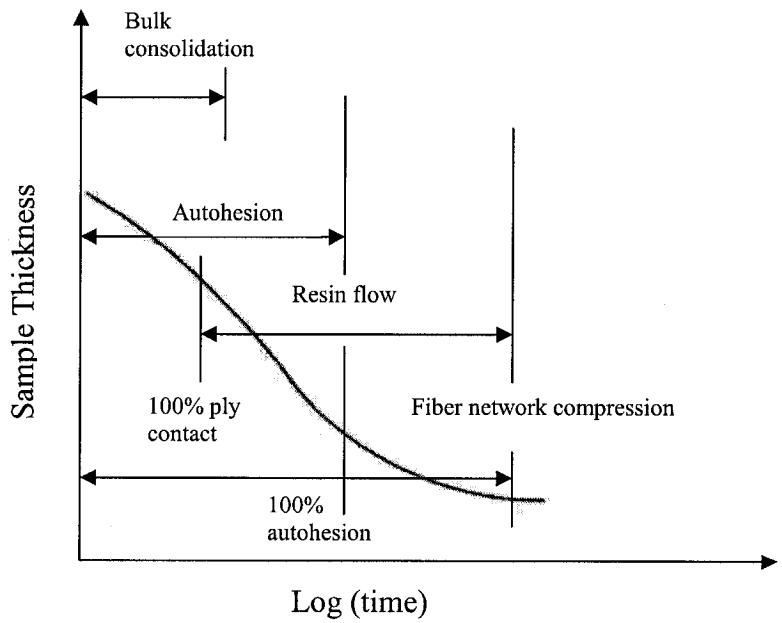


Figure 2.4: Decrease in thickness of a composite during consolidation [48].

Figure 2.4 illustrates the decrease in thickness as a function of consolidation time and indicates that several phenomena occur. When a thermoplastic prepreg layup is compressed above its melting temperature, the pressure brings the prepregs into intimate contact and eliminates any free spaces between the plies. This is accomplished by the later squeezing flow of the resin on the prepreg material and is completed when the extent of spatial gaps between the plies is minimized [48].

After the prepregs coalesce, matrix interfaces can adhere to one another by the molecular diffusion of the matrix. This healing process is called autohesion. Autohesion is defined as the diffusion of chain segments across an interface, leading to the elimination of the interfaces. Conversely, adhesion is due to the chemical bonding of two dissimilar materials at an interface [51]. While gaps between the prepreg plies are being squeezed closed, a portion of resin will experience a pressure gradient. This pressure gradient drives the resin to flow around and through the fiber bundles. Resin flow may redistribute the fiber bundles and deplete the composite of the matrix. If the fibers have not been completely prewet with the resin, as in commingled tows, this flow will produce resin permeation through the dry fibers and finally wet the fiber bundles.

If the applied pressure is reduced when the resin is still molten, the composite exhibits a significant elastic recovery (figure 2.5) [48]. In many practical situations, the fiber network is compressed to the point that it starts to take up a significant portion of the applied load. This elastic behavior may be more significant if the fiber form is a woven mat or a flexible tow.

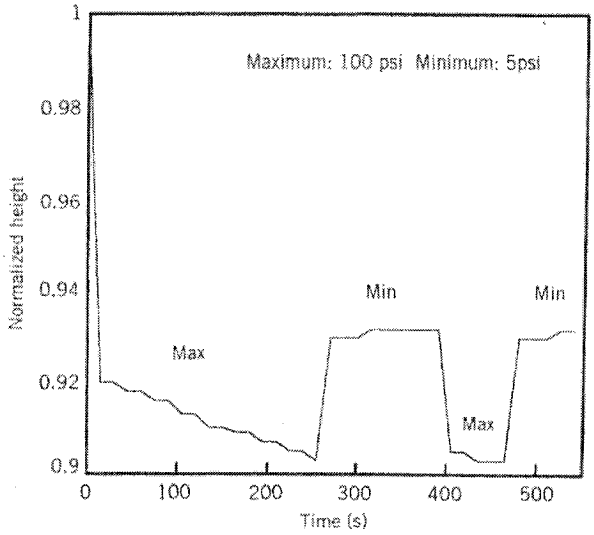


Figure 2.5: Elastic recovery of a thermoplastic composite on reduction of the applied load [48].

When the pressure is applied at the onset of consolidation, it is concentrated on developing intimate contact between plies. In figure 2.6, as consolidation continues, complete intimate contact is developed and area of intimate contact (A_{ic}) approaches total area (A_T). Eventually resin is squeezed out of the plies and the fiber network carries a larger portion of the pressure [48].

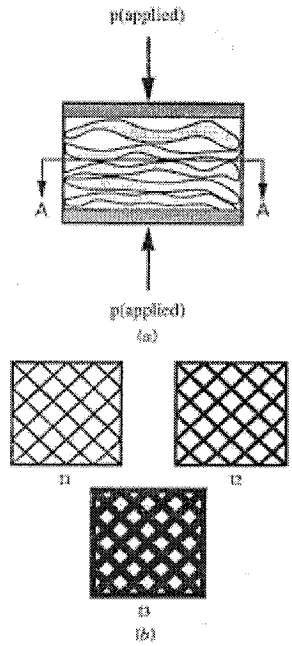


Figure 2.6: (a) Consolidation of Laminates (b) development of A_{ic} in section A-A during consolidation [48].

2.5.2.1 Bulk consolidation

Bulk consolidation is a phenomenon during which the individual prepregs are brought into intimate contact and the free space inside the laminate is eliminated. The mechanism of bulk consolidation is different for each type of prepreg. For tape prepreg, the prepreg is already fully impregnated and during consolidation spatial gaps only occur between plies because their surfaces are rough and uneven. The bulk consolidation of flexible towpregs is different from tape. Usually flexible towpregs are produced by a process that spreads and powder coats the continuous reinforcement fiber filaments with melt-fused thermoplastic particles. First, a flexible towpreg is not perfectly impregnated with the matrix. The flexibility of the towpreg makes intimate contact between the prepregs easy

and immediate. Even though intimate contact is accomplished in this towpreg, the incomplete impregnation of the matrix plays a major role in bulk consolidation.

Therefore, the bulk consolidation of flexible towpreg needs to include resin impregnation rather than intimate contact and can be explained by a resin flow model. Bulk consolidation is extremely important in processing these unconsolidated towpregs for techniques such as filament winding and tape laying because it is necessary first to decrease the bulk of the material in order to obtain autohesion. So bulk consolidation is a key concern when processing flexible towpregs and commingled tows.

2.5.2.2 Autohesion

After the spatial gaps in the laminate are removed, the diffusion of polymer chains takes place at the contact surface. This diffusion moves the chain ends of the polymer and they entangle neighboring chains. As contact time increases, the extent of chain entanglement increases and results in the formation of a strong bond at the interface. As the chain motion grows, the penetration length of the chain across the interface increases and the fracture toughness and the tensile strength of the interface are enhanced [48]. Wool [52] showed that mechanical properties such as stress, modulus, and impact energy, are related to time, temperature, molecular weight, and constitution of the material.

Bastien and Gillespie [53] explained that for online consolidation or compression molding process, where the two surfaces are brought in contact at a high temperature, the required contact time to obtain full strength is very close to the bulk consolidation time and the autohesion time is negligible.

Muzzy and Colton [48] presented that the contact time for perfect autohesion is directly proportional to the viscosity of the polymer and described by the equation 2.1

$$t_c = 22.9\eta \quad \text{.....(2.1)}$$

Where, t_c = contact time and η = viscosity of polymer in MPa-s.

The autohesion time can be ignored for relatively slow processes, such as compression molding, because the processing time is much greater than the autohesion time. For faster processes, such as filament winding, fiber placement, and pultrusion, the time of contact at high temperature and pressure is much shorter, and may be on the order of magnitude of the time for complete autohesion. In this case autohesion must be taken into account.

2.5.2.3 Resin flow

Deformation of composite is constrained by the fiber reinforcement but facilitated by the matrix, which acts in the form of a lubricant between individual fibers and between plies of different orientation.

Figure 2.7 illustrates the four basic flow deformation processes that may occur during the processing of prepregs into product forms [46, 54, 55]. The first two among these four processes are discussed below.

1. resin percolation through and along the fibers
2. transverse fiber flow (squeezing flow)
3. intraply shearing flow along the fiber direction (individual fibers)
4. interply slip-cooperative flow

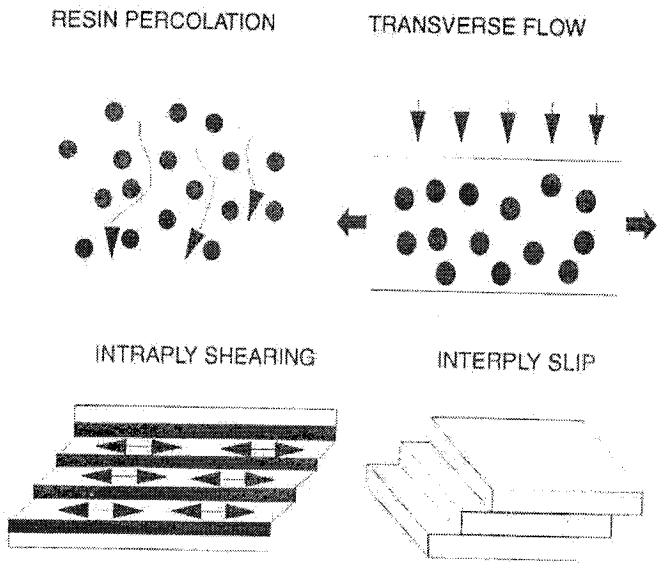


Figure 2.7: Flow mechanisms in preimpregnated products.

2.5.2.3.1 Resin percolation

Percolation heals any flaws in the structure and in particular, allows the bonding of different layers of preimpregnated tape. The bed of reinforcing fibers is anisotropic in nature and flow is possible both along and across the orientation axis of the fibers (figure 2.8).

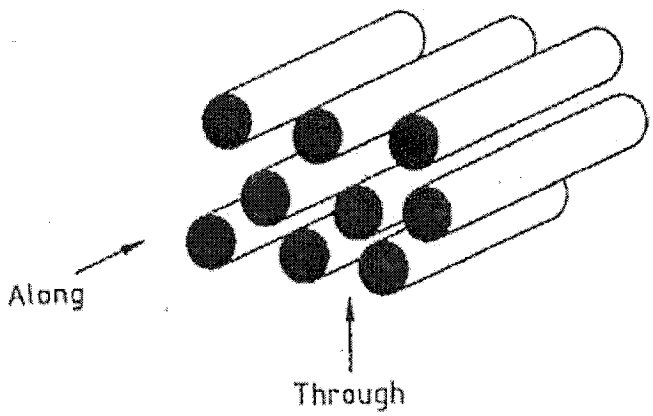


Figure 2.8 Anisotropic Permeability

At high fiber volume fractions percolation is much easier along the fibers because touching fibers essentially seal off the transverse flow. However, the resin flow path is usually long in the direction of fiber axis so that the apparent dominant flow process is across the fiber axis. Any transverse flow is likely to include local axial flow as the resin seeks out the path of least resistance. To achieve a full consolidation of a stack of plies with different orientations it is necessary to bleed a small amount of resin from each prepreg layer to form a resin rich interlayer. Such an interlayer can be formed within a matter of few seconds under pressure of 10 atm if the resin viscosity is within the range of 100-1000 Nsm^{-2} [54].

2.5.2.3.2 Transverse flow process

The application of normal force to a deformable material in a parallel plate plastometer results in a transverse flow, shown schematically in figure 2.9.

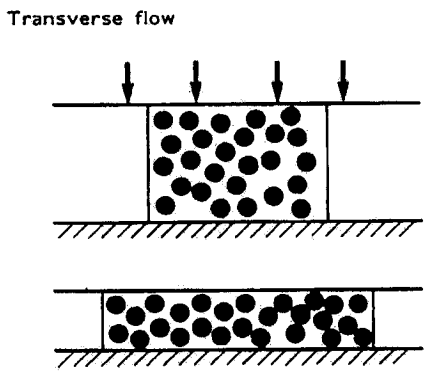


Figure 2.9: Compression of unidirectional composite.

A sample geometry is shown in figure 2.10 to explain this process.

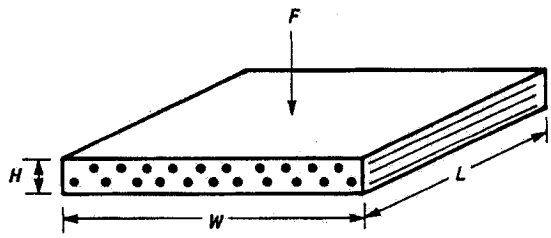


Figure 2.10: Sample geometry: F = applied force; W = specimen width across fibers; L = specimen length along fibers; and H = specimen thickness.

The application of normal force results in a pressure gradient within the material and it is this pressure gradient which induces transverse flow. There is pressure gradient both across the width (W) and along length (L) of the fibers as shown in figure 2.11. Because the fibers are inextensible, the sample cannot expand along the axis of the fibers (L) but resin can be squeezed out in that direction. Because there is a pressure gradient both across and along the fiber axis, the maximum pressure across the fiber axis necessarily occurs at the center of any length of fibers. This pressure distribution over the area of the sample leads to a flow which is represented qualitatively in figure 2.12.

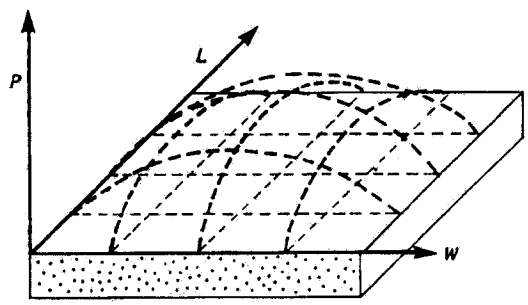


Figure 2.11: Pressure distribution during normal loading [54].

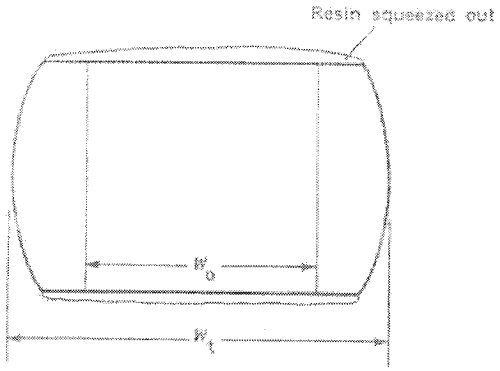


Figure 2.12: Barreling deformation and resin squeeze out [54].

In practice, there is some slight twisting in the fiber tows. This twisting is further exaggerated by the velocity gradients associated with the transverse flow process, as shown schematically in figure 2.13.

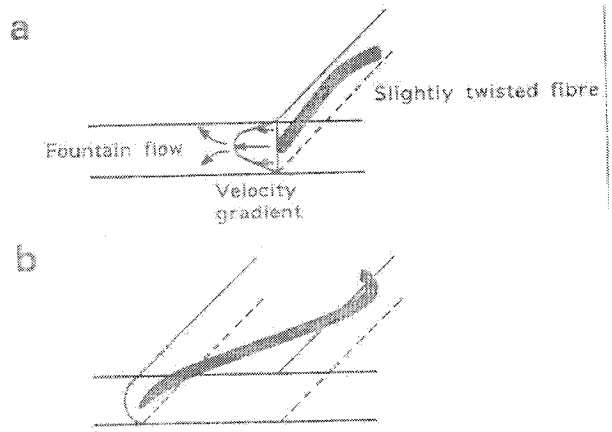
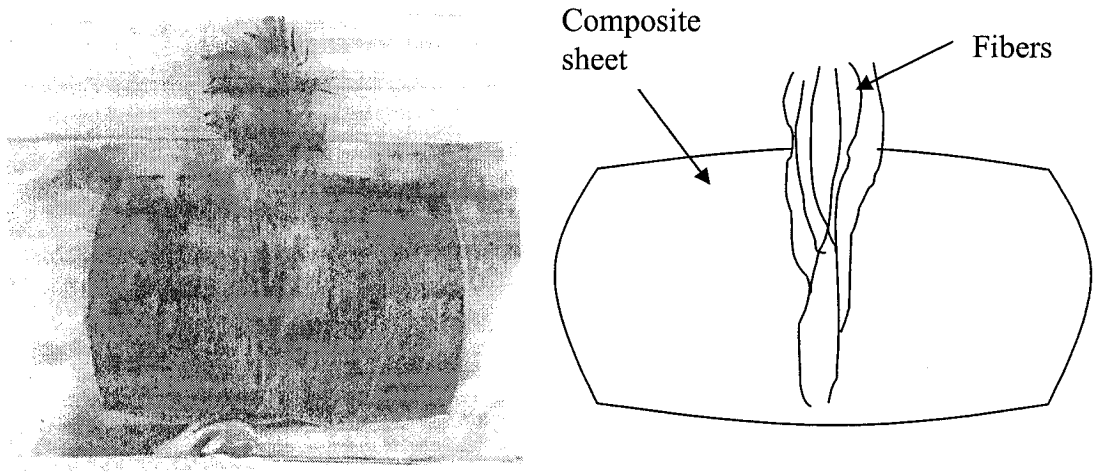


Figure 2.13: Exaggeration of fiber twisting by transverse flow [54].

The exaggeration of the fiber twisting by transverse flow tries to increase the length of the inextensible reinforcing fibers and this acts as an effective brake on the motion. After subjected to a transverse flow it was found that high level of distortion in those fibers which have flowed the greatest distance with relatively little distortion in the central

region of the specimen. The twisting of the fibers appears to produce an absolute limit in transverse flow as nominal applied pressure is increased. The limitation in transverse flow resulting from locking due to fiber twisting sets the scene for a dramatic instability. In thick samples at very high nominal pressures the fibers jet out axially in an unstable intraply deformation in the manner shown in figure 2.14 [54].



(a) (b)

Figure 2.14: (a) Fiber jetting in thick sheet [54]; (b) Schematic of fiber jetting in thick composite sheet.

It is noticeable from the figure that highly twisted fibers exist near the edges of the sheet. This jetting occurs in the center of the specimen where the fibers are least twisted. It is presumed that the trigger for this instability is a lack of true parallelism in the plates under very high loading [54].

2.5.2.4 Elasticity of fiber networks

During consolidation, the fiber volume fraction increases and the fiber network begins to take up an increasing amount of the applied load. In the extreme case, the fiber network carries the entire load and the resin pressure drops to zero. Therefore, the elastic behavior of the fiber network must be considered for a correct prediction of consolidation [48]. Gutowski and co-workers [56, 57] addressed fiber deformation by assuming that a composite is a porous, nonlinear elastic medium that is filled with a viscous resin. They modeled the deformation of bundles of fibers as beams bending between multiple contact points.

2.5.3 Solidification and crystallization

During solidification, the maintenance of pressure is required until the temperature of the composite is below its matrix's glass transition temperature. This restricts the nucleation of voids within the resin, suppresses the elastic recovery of the fiber network, and enables the composite to maintain the desired dimensions [48].

Crystallization has a significant effect on the mechanical properties and solvent resistance of the composites and results in crystallization shrinkage [58]. In addition to crystallization shrinkage, the difference in the coefficients of thermal expansion between the fibers and the resin lead to residual stresses and warping [17]. The residual stresses can be relieved partially during processing if the thermoplastic matrix is maintained near glass transition temperature or the cooling rate is controlled to provide an even temperature profile throughout the part.

2.6 Conclusion

In this chapter, the necessity of understanding the processing science has been discussed. An overall idea on various aspects of processing has been presented after understanding the advantages and disadvantages of thermoplastic composites over thermoset based composites. A detail discussion on different steps of consolidation as well as the flow patterns during consolidation has been described.

CHAPTER 3

MATERIAL AND EXPERIMENTAL METHODOLOGY

3.1 Introduction

One of the primary motivations for this work is to develop a cross-piece for the helicopter landing gear using PEKK based thermoplastic composite material. The implementation of this goal can only be achieved by making a work plan which incorporates the available research facilities for the investigation. For developing the final product, the very fundamental investigation, which is the objective of this thesis, must comply with the utilization of the available resources. In terms of manufacturing technology, Bell Helicopter Textron Canada Limited has the intention to fabricate the final product using in-situ fiber placement technology. Keeping that in mind, a preimpregnated form of material such as unidirectional prepreg tape is an obvious selection for this research.

The content of this chapter includes the description of the material that has been used for this work. It also focuses on the detail experimental methods those are adopted throughout the entire investigation.

3.2 Material

The material used for this work was Carbon fiber reinforced PEKK preimpregnated tape. PEKK thermoplastic polymer was first developed in 1980s by E. I. du Pont de Nemours & Company Inc. [19], USA. But the manufacturer and supplier of material for the project was CYTEC Engineered Materials, USA.

3.2.1 PEKK Properties

PEKK is a semi-crystalline thermoplastic polymer which exhibits lower melt viscosity than PEEK rendering the processing and the achievement of optimum consolidation of fiber reinforced composite laminates easier [43]. PEKK shows excellent thermal stability, low moisture absorbance and excellent flammability resistance. The high toughness and tensile modulus of PEKK contributes to its high composite performance [19, 42, 43]. PEKK has a glass transition temperature, T_g of 156°C and melting temperature, T_m of 305-310°C.

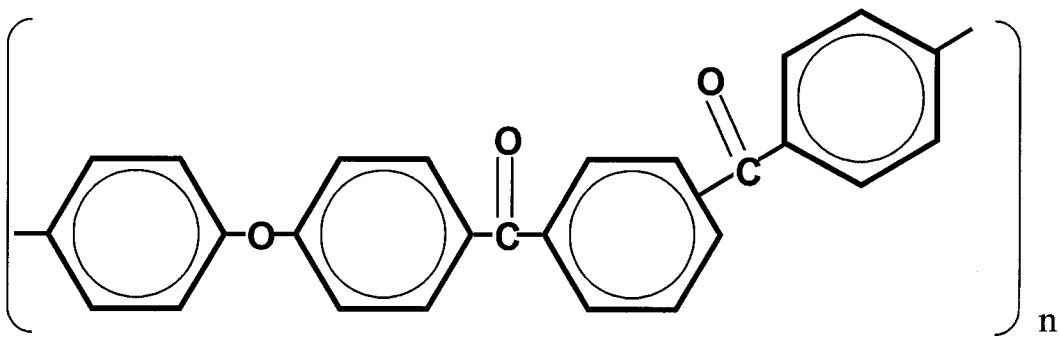


Figure 3.1: Chemical structure of PEKK polymer [19].

The properties of neat PEKK resin and other thermoplastic resins are shown in table 3.1 [19].

Table 3.1: Neat PEKK resin properties [19].

Property	*Unit*	*PEI*	*PPS*	*PEEK*	*PEKK*
Density	g/cm^3	1.27	1.35	1.32	1.29
Tensile Strength	MPa	105	90	100	90
Tensile Modulus	GPa	3.0	3.8	3.5	3.4
Elongation at Failure	%	60	3	60	80
Flexural Modulus	GPa	3.3	3.8	4.0	3.3
Flexural Strength	MPa	152	96	170	138
Notched Izod Impact Strength	J/m	53	16	60	48

3.2.2 Prepreg Tape

The supplied unidirectional pre impregnated tape of Carbon/PEKK has a resin content of 34% by weight [19]. The tape is supplied in a roll and the width of tape is 304.8 mm (12 inch). The thickness of the tape before consolidation is 0.15 mm (0.0059 inch). Figure 3.2 illustrates the prepreg tape before molding.

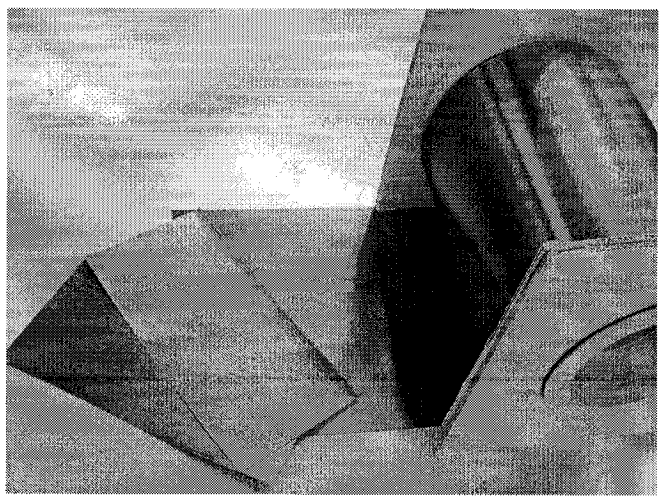


Figure 3.2: Carbon/PEKK unidirectional prepreg tape.

3.3 Laminate Manufacturing

3.3.1 Manufacturing Technique

Flat laminates from Carbon/PEKK prepreg tape are manufactured by using a compression molding technique. Compression molding is a simple processing technique consisting of placing the thermoplastic prepreg plies inside a heated mold located between two platens of a hydraulic press. Pressure is applied as the material melts. Once the polymer is molten, it takes only seconds to fuse under heat and pressure. Processing time, mostly due to the heat up and cool down requirements, is short.

This technique is widely used because of its convenience. The dies, usually made of metal, are precisely machined to provide a uniform consolidation pressure. If a mismatch in thickness between the composite part and the die should exist then non-uniformity in pressure and heat transfer will occur resulting in a non-uniform consolidation. Pressure uniformity can be improved by incorporating a compliant layer between platens of the press and the stack of plies [3].

For the experiments of this work, a Wabash Press is used. It is a 30 ton capacity heated press with a temperature range up to 1000°F (538°C) and integrated water and/or air cooling system. Figure 3.3 illustrates the Wabash press used for laminate manufacturing.

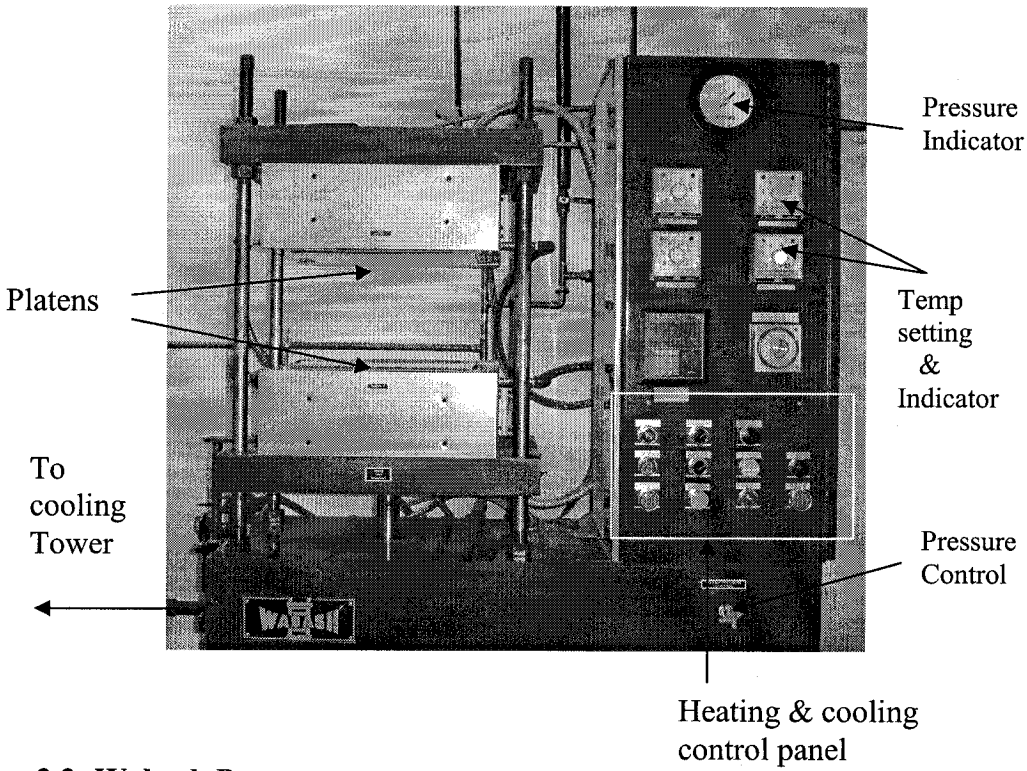


Figure 3.3: Wabash Press.

3.3.2 The Mold

To incorporate uniform pressure distribution, dimensional stability and better surface finish – a steel mold (figure 3.4) has been designed to fabricate laminates from prepreg plies. The mold has two steel side frames which hold and inhibit sliding of the prepreg plies in between when closed from the sides. Another function of the side frames is to provide the thickness uniformity of the laminate. The top and bottom plates, when put together with the side frames and prepreg plies, prevent any movement of the frame and the laminate with the application of pressure; assure the uniform pressure distribution to the laminate and restrict any spring back phenomena when the pressure is removed after the consolidation cycle.

The length of the mold is 355.6 mm and the width is 203.2 mm (L = 14 inch and W = 8 inch) with an area of 304.8 mm × 152.4 mm (12×6 inch^2), enclosed by the side frames, to hold the prepreg plies. The thicknesses of the two steel plates are 6.35 mm (0.25 inch) each. The side frames are 25.4 mm (1 inch) in width at all sections and have thicknesses of 1.1 mm (0.043 inch).

Appendix – A has the detail drawings of the mold.

Figure 3.5 depicts the schematic of the cross-section of the mold when the prepreg plies are placed in between.

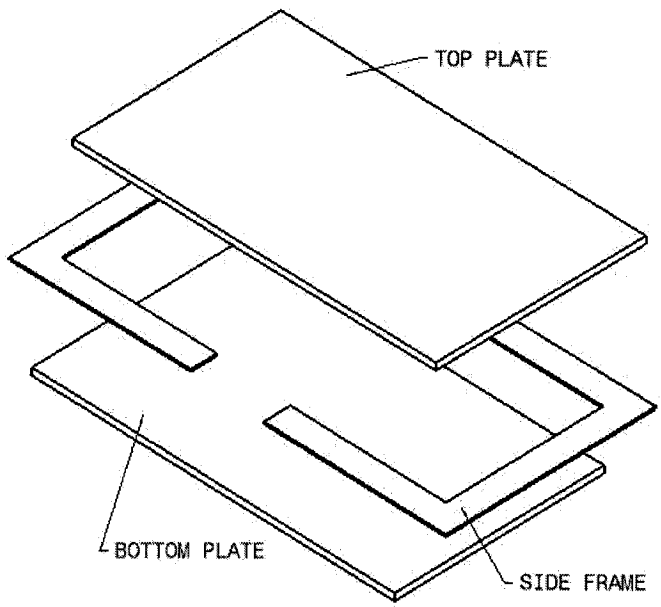


Figure 3.4: Steel Frame mold used for laminate manufacturing.

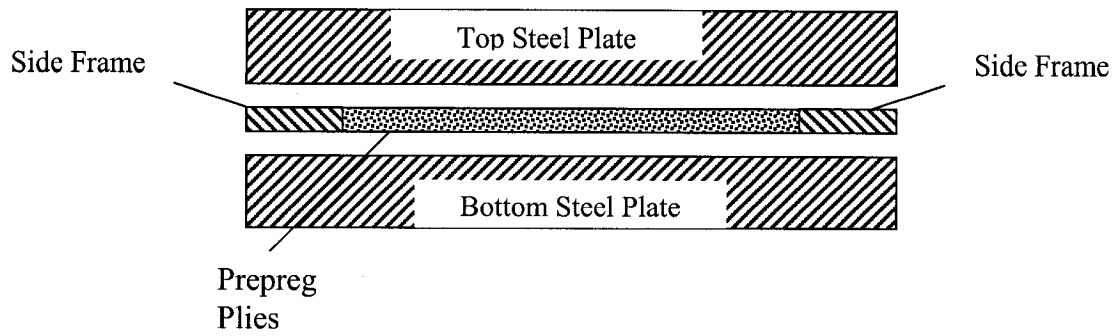


Figure 3.5: Schematic of the cross-section of the Steel frame mold with prepreg plies in between.

3.3.3 Laminate configuration

Unidirectional tape prepreg plies of Carbon/PEKK are used in this study to fabricate laminates by consolidating in a multi-ply sequence. In order to determine two of the primary elastic constants (Young's Modulus – E_1 and E_2) for an anisotropic material, laminates with two distinct configurations are necessary. Based on this fact, laminates with 0° (axial) and 90° (transverse) ply orientation are fabricated separately.

3.3.4 Specimen preparation

Carbon/PEKK unidirectional tape prepreg plies are cut from the roll in lengths of 304.8 mm (12 inch) and widths of 152.4 mm (6 inch) to fit inside the area enclosed by the two side frames, in the mold. 8 pieces of these plies are stacked in a multi-ply sequence to fabricate one laminate. The mold is cleaned very carefully with sand paper in order to remove any foreign particles on the surface and cleaned with acetone before application of release agent. Release - All # 50® (manufactured by Airtech International Inc., USA) - a high temperature resistant liquid release agent is applied to the side frames and to the

inner two faces of the top and bottom plates of the mold. The reasons for the application of release agent are to prevent the permanent accumulation of any excess resin on the mold surface and to facilitate smooth tool release. Once the mold is prepared, the plies are wrapped along the length direction with a high temperature polyimide film (Kapton® - a registered trademark of Du Pont), which works as a dam inside the mold to restrain the transverse flow of the resin out of the mold during consolidation cycle; also to ensure a better surface finish of the final laminate. The wrapping keeps the two axial end sides of the laminate open and facilitates bleeding of any excess resin during consolidation. Figure 3.6 demonstrates the schematic of the cross-section of the plies wrapped with Kapton® film. In practice, the Kapton® film is wrapped tightly to conform to the laminate surface.

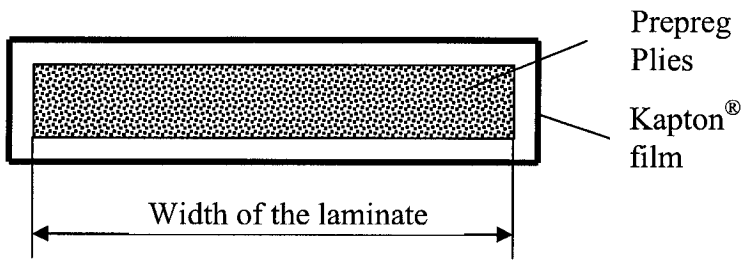


Figure 3.6: Schematic of the cross-section of the stacked plies wrapped with Kapton® film.

Thermocouples are placed at the mid section of the laminate to track the temperature for the whole period of consolidation cycle. The temperature tracking is achieved with the help of a National Instrument Data Logger system.

3.3.5 Consolidation parameters

Pressure, temperature, time and cooling rate – these are the four parameters that primarily affect the consolidation quality of a laminate [3, 59]. For the entire processing cycle - i) pressure, temperature and time, and ii) cooling rate are determined and employed for the consolidation and solidification stages respectively. The parameters used for the fabrication of the laminates in this study are listed in table 3.2.

Table 3.2: Consolidation parameters

Time, min	Temp., °C	Pressure, MPa (psi)				Cooling Rate, °C/min
			Contact Pressure	Consolidation Pressure	Solidification Pressure	
10 and 15	325 and 345	Set 1	0.48 (70)	1.38 (200)	1.72 (250)	7 to 10
		Set 2	0.48 (70)	1.72 (250)	2.07 (300)	

The pressure during the whole processing cycle is applied in three steps – contact pressure, consolidation pressure and solidification (cooling) pressure. The consolidation time indicates the dwell time when the temperature and pressure attain a value indicated in table 3.2. It remains constant and allows the melted resin to flow and wet the fibers completely. At a prior stage of this work, some laminates were fabricated using the contact and consolidation pressures only. No solidification pressure was applied and hence the resulting laminate contained more voids as observed during microstructural study. These prior experiments helped in selecting the final parameters listed in table 3.2 to optimize the consolidation quality. In addition to the experimental interpretation, the reference from CYTEC [19] was also used as a guide to determine the consolidation parameters.

3.3.6 The Molding cycle

The Wabash press platens are closed and preheated to 285 – 290°C before the mold assembly is placed in between the platens. Once the mold assembly is placed in between the platens at the temperature mentioned above, a contact pressure is applied to ensure the intimate contact between plies. The consolidation cycle then follows the pressure temperature and time profile as shown in figure 3.7.

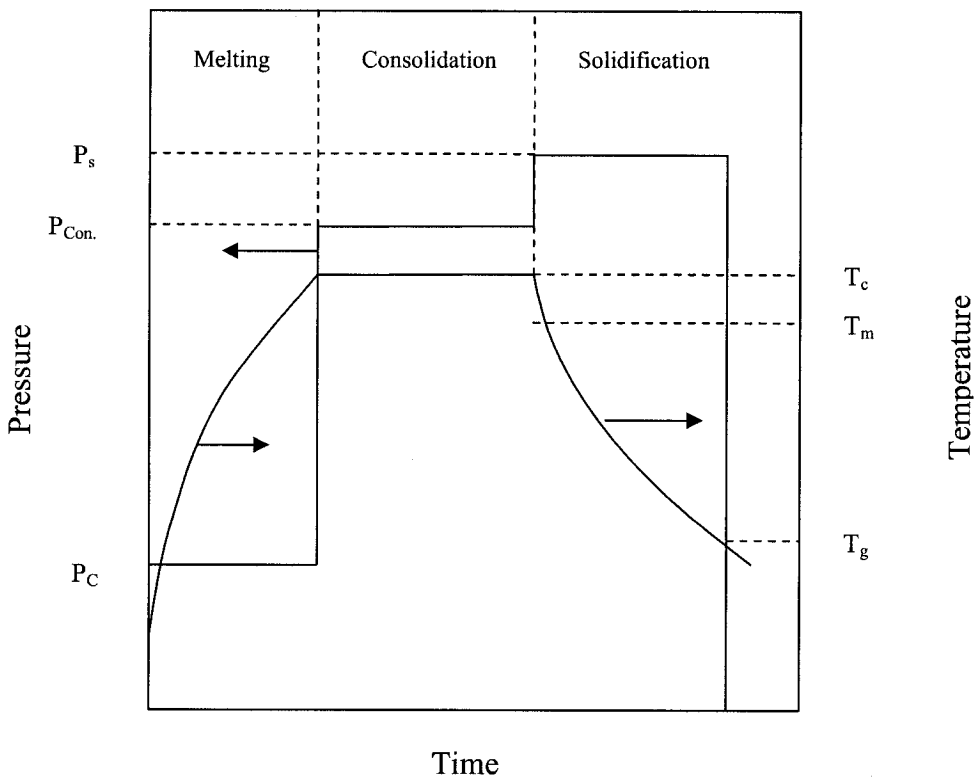


Figure 3.7: Pressure-Temperature-Time profile for consolidation of laminates.

Upon reaching the consolidation temperature T_c, a consolidation pressure P_{con} is applied and kept constant for a certain amount of time, known as dwell time. The heating is then controlled to keep the temperature constant throughout the whole dwell time. As the

dwell time ends and the solidification (cooling) cycle begins, the pressure is increased to a higher amount, defined as solidification pressure P_s. This slight enhancement of pressure during cooling cycle was previously used by CYTEC [19] for fabricating laminates from Carbon/PEKK prepreg tape.

This increase augments the prevention of nucleation of voids and elastic recovery of fiber network [59]. This pressure remains steady till demolding is done at a temperature that is a little lower than the glass transition temperature T_g of the resin. It is noteworthy that at a preliminary stage of this work, it has been found that keeping the pressure same as the consolidation pressure up to demolding results in laminates with a higher amount of void content and eventually yields inferior mechanical properties.

Upon demolding from the press platens, the laminate is carefully released from the mold assembly and the Kapton® film wrap. Afterwards, it is cut into preferred sizes using a diamond cutter and set aside for exploration of laminate properties.

3.4 Laminate properties

Laminate properties were achieved in previous works [32, 36, 60] by exploiting several effective methods. Hou et al. [60] and Lebel et al. [36] determined the impregnation and consolidation quality by observing the microstructure, investigating the void content and examining the mechanical properties of the laminates. Hou established a relation between consolidation and mechanical properties of the laminates. Oya and Hamada [32] utilized SEM observation as a measure to observe the fracture surfaces of the laminates after failure from different mechanical tests. In this study, finished laminate properties are

investigated by observing the microstructure, determining the percent crystallinity and exploring the mechanical properties. These methods are adapted for all the laminates; those fabricated employing different processing parameters. The preparation of samples for the above mentioned methods is presented in this section.

3.4.1 Samples for Microstructural Observation

Before conducting the thermal and mechanical property investigations, test specimens are checked for distribution and wetting of fibers and for any defects, such as voids. Voids could develop as a result of trapped air inside the prepreg plies because of insufficient pressure during consolidation [59]. To observe all of these, a microstructural study is conducted. Since the specimens for microstructural study are quite small, the region of interest is cut into small size, usually 25.4 mm × 25.4 mm, and then immersed in a cup containing epoxy curing system. The curing system is prepared using EPON 828 and a hardener EPICURE 3046 with a mixing ratio of 1:0.47. The cup is then kept at room temperature for 24 hours for the resin to cure and harden. This in turn creates a bigger surface and hence a better grip for polishing the tiny specimen. Now the surface generated is polished with the grinding operation by means of a LECO VP – 150 automatic grinding machine. Six specimens are mounted in a holder and ground at the same time. Initially, specimens are ground with 320 grit SiC paper and subsequently with SiC papers that have 600 and 800 grit levels. Then the specimens are polished with 3 micron and 1 micron diamond suspension and finally with 0.05 micron SiC suspension to obtain a very smooth surface for microstructural analysis. It is noteworthy that during grinding and polishing operation, care is taken to maintain a perfect horizontal surface.

Two specimens from each laminate are studied under an optical microscope (OLYMPUS BX51M) and also by using Scanning Electron Microscopy (SEM) at different magnifications.

3.4.2 Differential Scanning Calorimetry (DSC)

The purpose of the study of DSC is to comprehend the thermal transitions of a polymer when heated. For a semi-crystalline polymer, the thermal transitions include glass transition and melting of the crystalline part of the polymer.

In the most popular DSC design, schematically shown in figure 3.8, two pans sit on a pair of identically positioned platforms connected to a furnace by a common heat flow path.

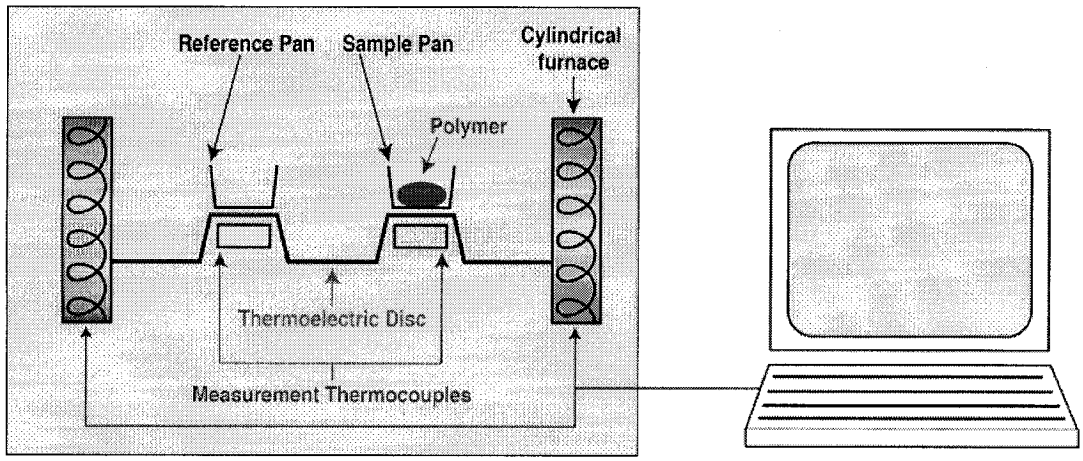


Figure 3.8: Schematic of DSC experimental setup.

In one pan, the polymer sample is kept. The other one is the reference pan which is empty. The whole process is controlled by a computer program where all the variables of the experiment are defined. After defining a heat flow rate, the furnace is turned on to

heat the two pans at the defined specific rate, usually something like 10°C per minute. The heating rate stays exactly the same throughout the experiment. But more importantly, the controller makes sure that the two separate pans heat at the same rate. The simple reason for this is because one pan has polymer in it, and the other does not. The polymer sample means there is extra material in the sample pan, indicating that it will take more heat to keep the temperature of the sample pan increasing at the same rate as the reference pan. This extra amount of heat is measured in a DSC experiment.

A plot of heat flow versus temperature is produced by executing the experiment. The resulting thermogram is then analyzed to determine the following [61]:

T_g = Glass Transition Temperature = The temperature (°C) at which an amorphous polymer or an amorphous part of a crystalline polymer goes from a hard, brittle state to a soft, rubbery state.

T_m = melting point = The temperature (°C) at which a crystalline polymer melts.

ΔH_m = the amount of energy in (Joules/gram) a sample absorbs while melting.

T_c = crystallization point = is the temperature at which a polymer crystallizes upon cooling.

ΔH_c = the amount of energy (Joules/gram) a sample releases while crystallizing.

These data can be used to determine the percent crystallinity that exists in the polymer before testing. Equation 3.1 is used to calculate the crystalline fraction present in a polymer.

$$\text{Crystalline fraction} = \frac{m_c}{m_{total}} \quad \text{.....(3.1)}$$

Where,

m_{total} = weight of the sample inside the aluminium pan.

$m_c = \frac{H'}{H^*_m}$; $H' = (\Delta H_m - \Delta H_c) \times$ mass of sample;

H^*_m = specific heat of melting (J/g).

A typical DSC plot for a semi-crystalline polymer will be as shown in figure 3.9. Completely amorphous polymers do not show any crystallization or melting.

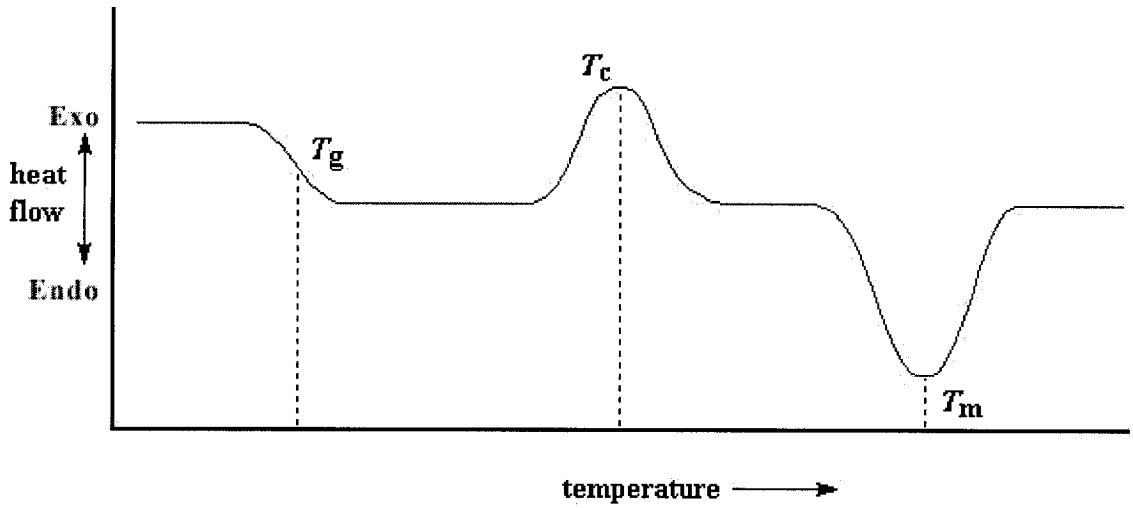


Figure 3.9: Typical DSC curve for a semi-crystalline polymer.

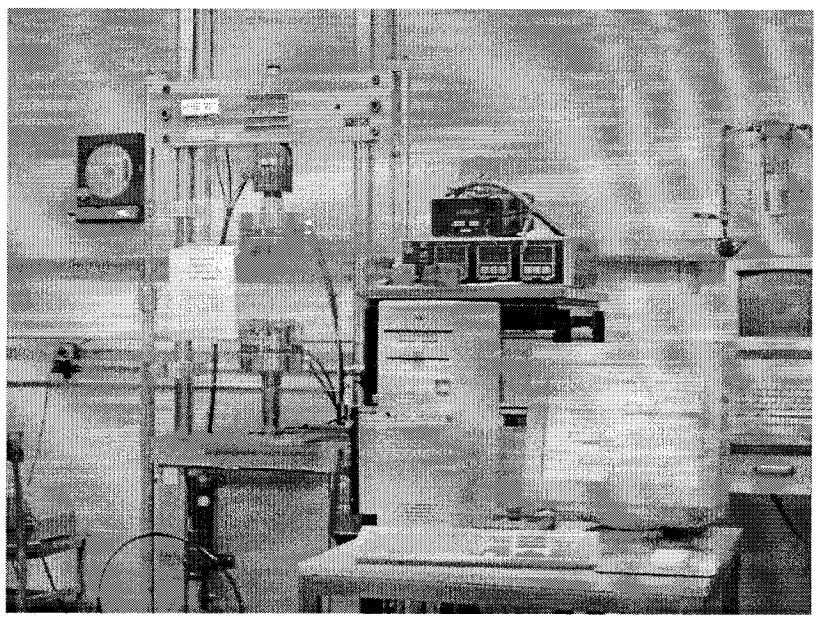
In this study, DSC experiments are performed to determine the glass transition temperature, melting temperature, crystallization temperature and percent crystallinity of the polymer in the consolidated laminates.

For the experiments of this work, a PERKIN ELMER PYRIS 1 Differential Scanning Calorimeter was used. A sample of 5 to 7 mg, is cut from the laminate into very tiny pieces containing both polymer and fibers. It was placed in an aluminum sample pan and the experiment was executed. From the thermogram of the experiment, the required

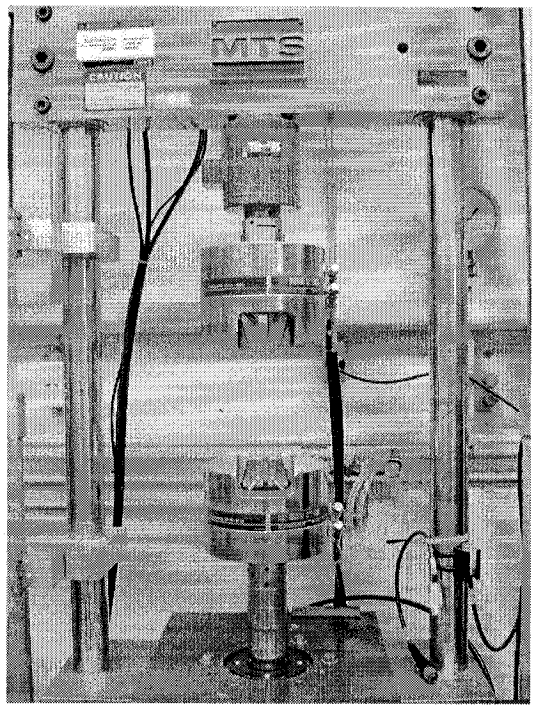
quantities (glass transition, crystallization and melting temperatures and percent crystallinity) are obtained and calculated. In order to acquire the correct amount of crystallinity in the polymer, neglecting the effect of fibers inside the sample, the total mass of the polymer used in equation 3.1 is multiplied by the weight fraction of the polymer in the prepreg tape. The specific heat of melting for PEKK polymer, as provided by the manufacturer, is 130 J/g. Each experiment is performed twice to confirm repeatability of the results.

3.4.3 Mechanical Testing

Tensile strength and modulus for the consolidated laminates are determined in both axial and transverse directions. Experiments are performed on an MTS universal tensile testing machine having a loading capacity of 10 KN. Figure 3.10 shows the experimental setup for tensile testing of the laminate coupons.



(a)



(b)

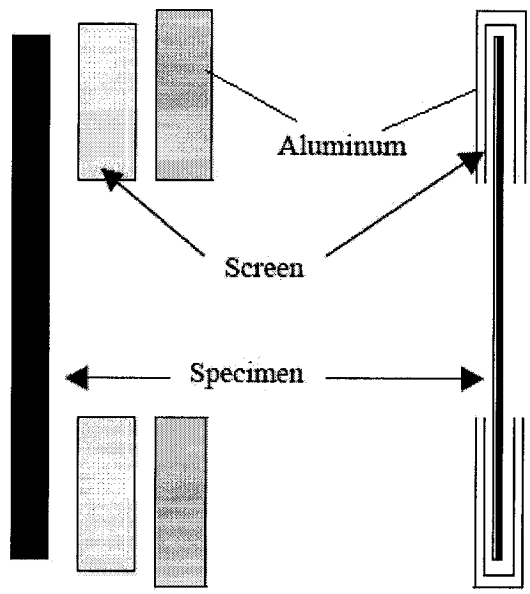
Figure 3.10: Experimental set-up for tensile testing of laminate coupons; (a) the complete set-up (b) the grips.

The tests are conducted in accordance with ASTM D3039 procedure. All testing was carried out at room temperature. The experiments are performed in displacement control at a specified constant displacement rate which is set to 1 mm/min. Strain gages are used to measure the strain which is used to calculate the modulus of the specimens.

The average length, width and thickness of the specimens are 254 mm, 12.7 mm and 1 mm for axial (0°) laminates and 180 mm, close to 25.4 mm and 1 mm for transverse laminates (90°) respectively.

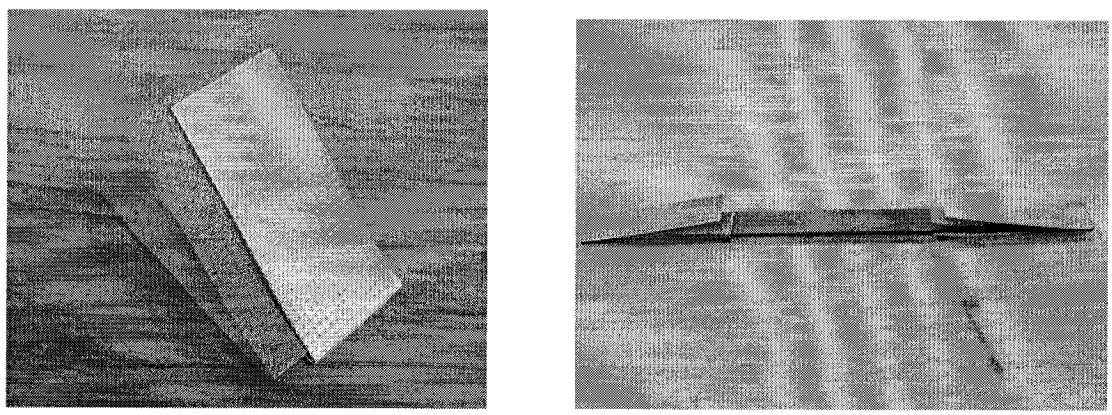
Specimens are tabbed to improve gripping in the load frame and reduce damage caused by the grip wedges. The tabbing material [62] used consisted of 100 count (100 wires per linear inch) stainless steel screen and aluminium sheet which has a thickness of 0.48 mm. Both the screen and aluminium sheet are cut into a rectangle of 12.7 mm (width) by 127

mm (length) for axial laminates and 25.4 mm by 50.8 mm for transverse laminates. Then they are folded in half around the two ends of the specimens as shown in figure 3.11. The sequence of tabbing assembly is also illustrated in figure 3.12.



(a) (b)

Figure 3.11: Schematic of Tensile test specimen and tabbing; a) front: pre-assembly b) side: assembled.



(a) (b)

Figure 3.12: (a) Sequence of assembly of tabbing material (b) assembled tab.

These tabs are very effective in preventing the slippage of the specimens from the grip during the tensile testing. The tab assembly also inhibits squashing of specimen in the tab area because of the gripping pressure. This is illustrated in figure 3.13.

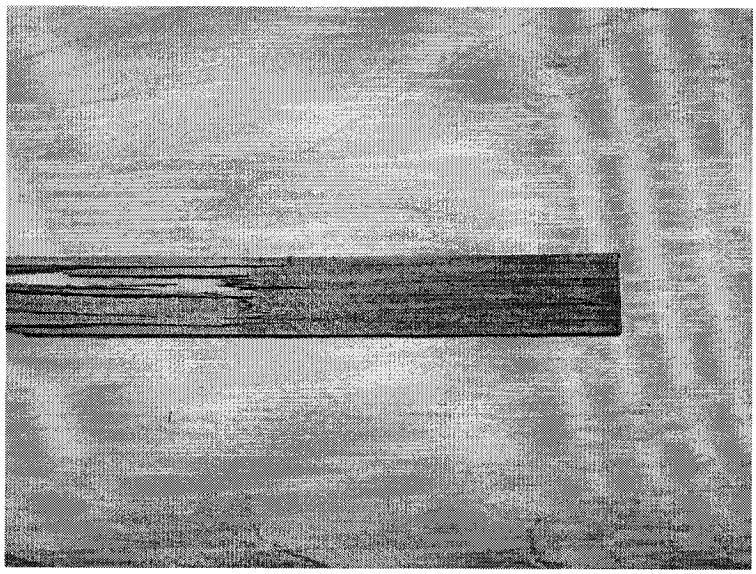


Figure 3.13: Undamaged tabbing area after failure of specimen.

The undamaged tabbing area assures no premature failure of the specimen which could initiate from the tab region because of cracks developed from gripping pressure.

3.5 Conclusions

Detail information on the Carbon/PEKK prepreg tape and the neat PEKK polymer itself are presented. The neat polymer property of PEKK is compared with few of the counterparts. The laminate manufacturing technique employed in this work is discussed in detail. This includes the mold design, the specimen preparation, consolidation parameters and the molding cycle. Finally, the experimental methodologies adopted to

determine the consolidation quality are presented. These methods include procedures of preparing samples and testing for microstructure observation, DSC analysis and mechanical testing. The methodologies described in this chapter are strictly followed to obtain the results presented in the subsequent chapter.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Introduction

Different consolidation parameters used in fabricating the laminates are presented in this chapter. Results of DSC analysis and mechanical tests are also presented. Because of the variations in the processing parameters, the subsequent changes in the consolidation quality of laminates are interpreted and discussed in the following sections. The consolidation quality of the laminates is verified by means of qualitative microstructural observation, amount of crystallinity present in the polymer and mechanical property evaluation. The discussion includes the comparison of different laminate properties pair by pair in terms of change in consolidation temperature, pressure and time. This chapter also includes the discussion on the effects of the processing parameters on the final properties of the laminates.

4.2 Consolidation Quality

The consolidation quality of the laminates is determined by microstructure observation, DSC analysis and mechanical testing. Researchers [19,42] have utilized different processing parameters to manufacture Carbon/PEKK laminates from tape prepregs. Keeping those references in consideration, eight different combinations of processing

parameters are determined and applied to verify the effects of these parameters to the final laminate quality. These parameters are listed in table 4.1. Two different temperatures, two sets of pressures and two different times are combined to define the consolidation parameters. One of the selected temperatures is close to the melting region and the other one is around the mid point of the processing temperature range.

A contact pressure (figure 3.7) is applied to bring the plies into intimate contact prior to melting and an increase in pressure during cooling cycle is employed to enhance the prevention of nucleation of voids and elastic recovery of fiber network [59].

Table 4.1: Consolidation Parameters for all laminates.

Sample #	Time, min	Temp, °C	Pressure, MPa		
			Contact Pressure	Consolidation Pressure	Cooling Pressure
CP1	15	345	0.48	1.72	2.07
CP2	15	325	0.48	1.72	2.07
CP3	15	325	0.48	1.38	1.72
CP4	15	345	0.48	1.38	1.72
CP5	10	325	0.48	1.72	2.07
CP6	10	345	0.48	1.72	2.07
CP7	10	345	0.48	1.38	1.72
CP8	10	325	0.48	1.38	1.72

4.2.1 Microstructure observation

A qualitative observation of the cross section of the laminates is performed to check the quality of the consolidation. In both optical microscope and SEM, the cross sections have revealed the distribution of fibers, voids (if any), resin rich areas and any other defects. The results of microstructure observation are presented in a following section where the results are compared pair by pair.

4.2.2 DSC Analysis

Finding the percent crystallinity of the laminates has helped to understand the effects of variable consolidation parameters in a quantitative way. From the average results of the DSC, the glass transition temperature is found to be 154.24°C, the melting temperature 303.10°C and crystallization temperature 239.20°C, which are in the proximity of the results provided by the manufacturer. Table 4.2 lists all these temperatures found from the experiments.

Table 4.2: Glass transition, crystallization and melting temperatures of Carbon/PEKK laminates.

Sample #	Glass Transition Temperature, °C	Crystallization Peak Temp. °C,	Melting Peak Temperature, °C
CP1	151.05	205.83	301.16
CP2	156.84	241.66	303.83
CP3	154.03	243.50	306
CP4	153.68	237.5	302.83
CP5	154.06	240.16	301.83
CP6	156.24	268.83	303
CP7	154.64	238.5	302.83
CP8	153.40	237.66	303.33
Average	154.24	239.20	303.10

The range of cooling rate was 7-10°C/min. The crystallinity in the laminates ranges from 8% to 16%. The final mechanical properties of the laminates reflect the changes of crystallinity along with the microstructural variation. Figures 4.1 to 4.8 show the DSC thermograms obtained from all the experiments. The first transition (change in slope) on any one of the curves is the change in the specific heat of the polymer and the mean value of the slope gives the glass transition temperature of the polymer. The next change in the

curve after glass transition is the crystallization dip. The dip area gives the total heat released by the polymer during break down of the crystals. The final change in the curve is the melting peak and the area under it gives the amount of heat absorbed by the polymer during melting. All these values obtained from the curve are applied in equation 3.1 to calculate the percent crystallinity of the polymer and listed in table 4.3 for all the laminates.

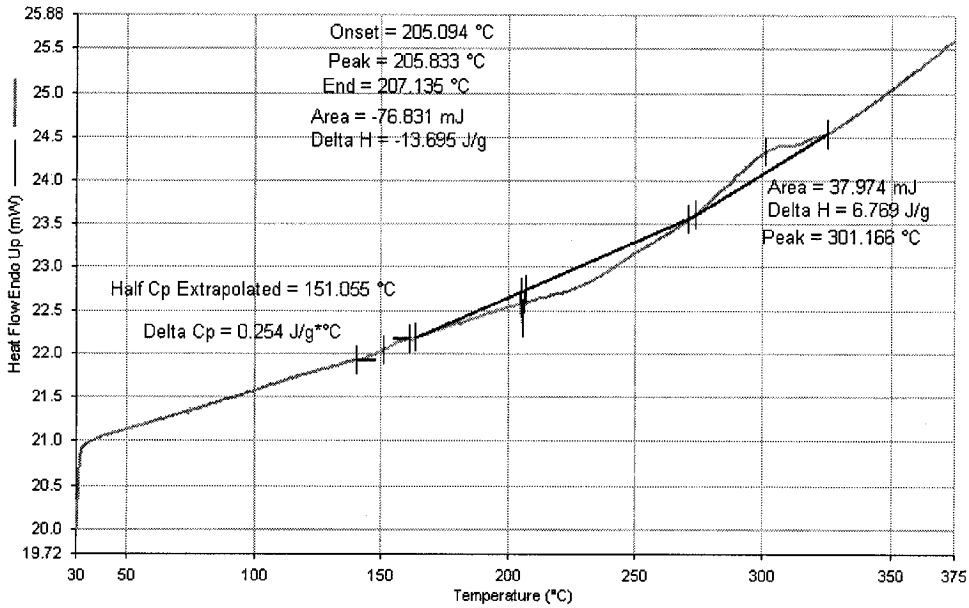


Figure 4.1: DSC thermogram of CP1 laminate.

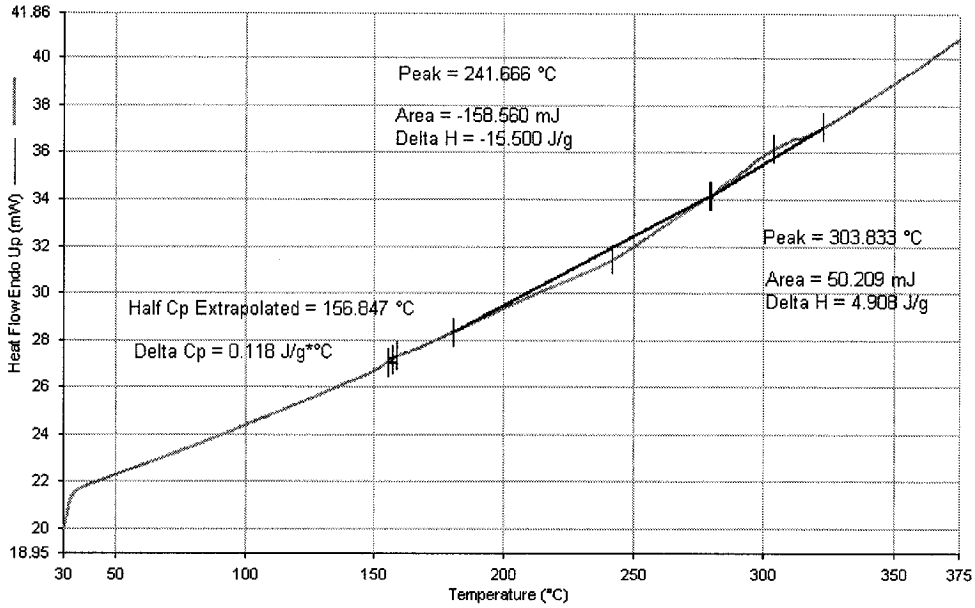


Figure 4.2: DSC thermogram of CP2 laminate.

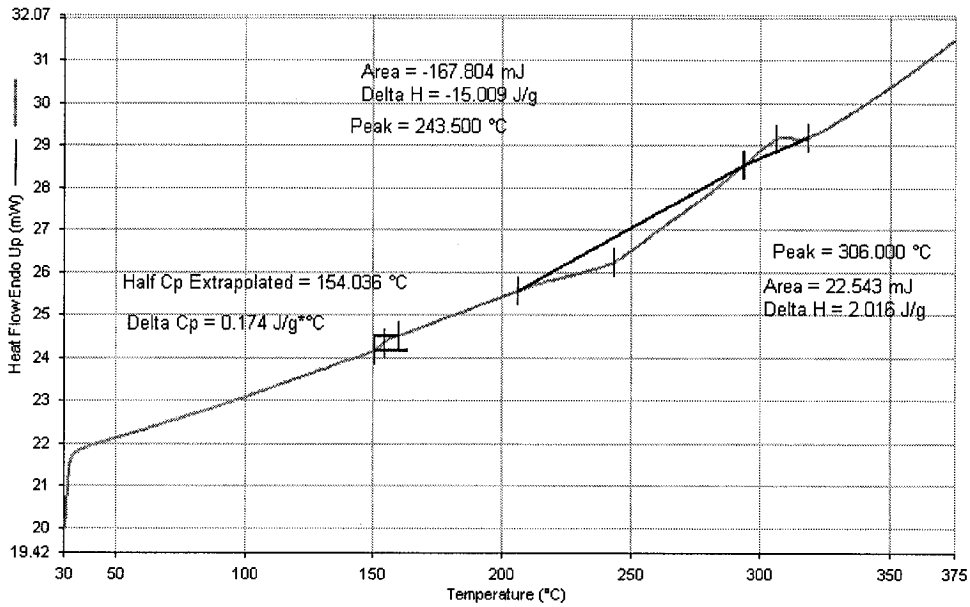


Figure 4.3: DSC thermogram of CP3 laminate.

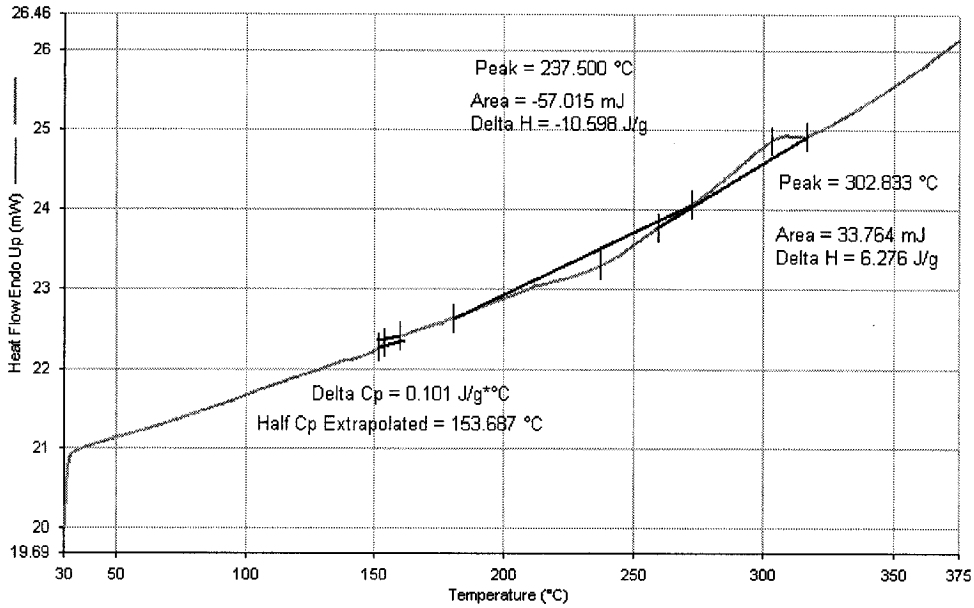


Figure 4.4: DSC thermogram of CP4 laminate.

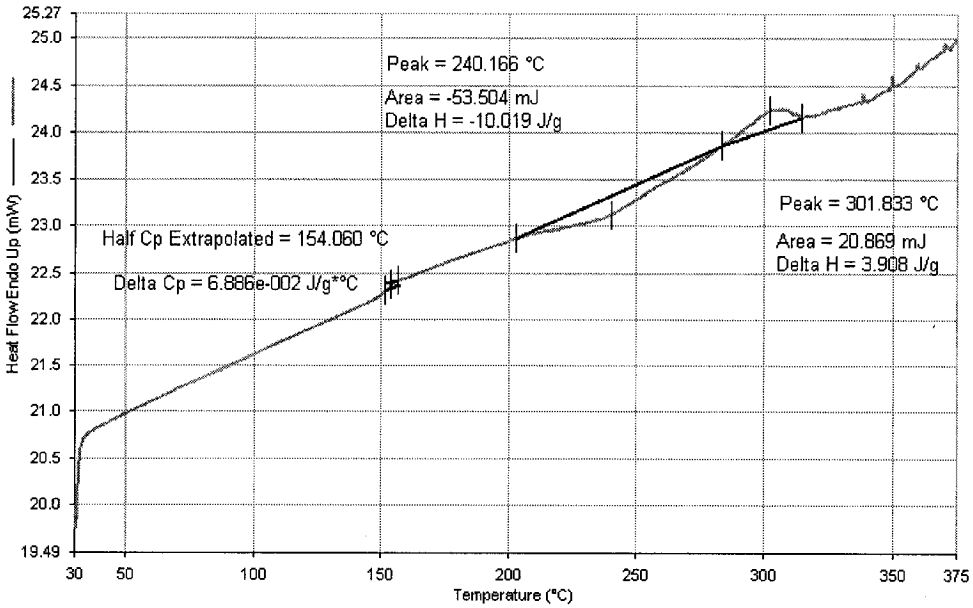


Figure 4.5: DSC thermogram of CP5 laminate.

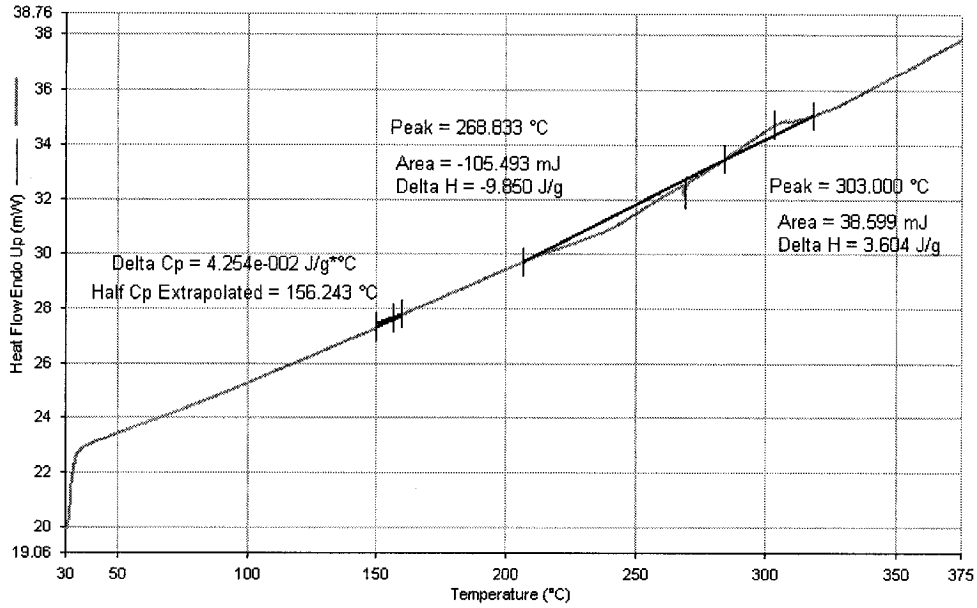


Figure 4.6: DSC thermogram of CP6 laminate.

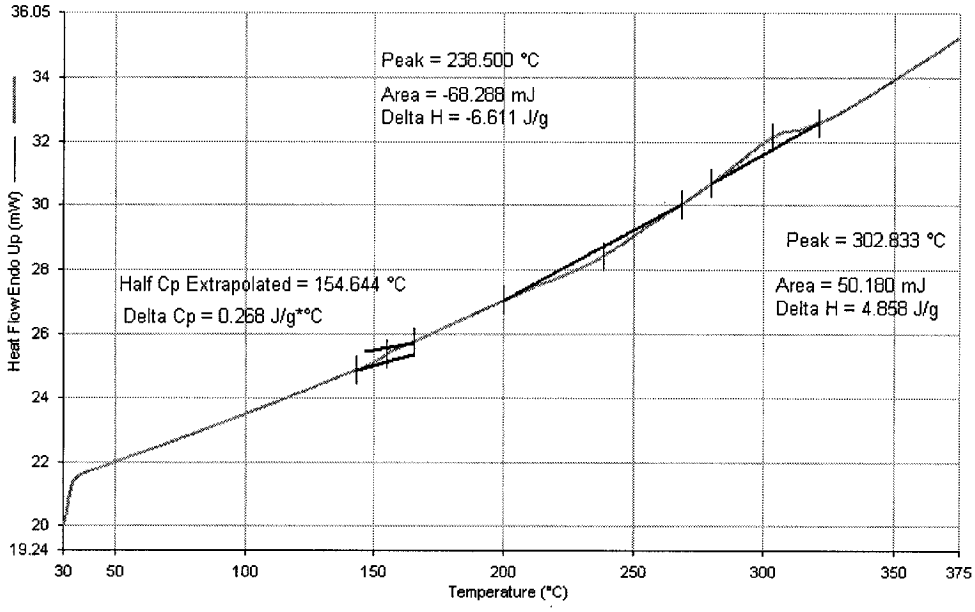


Figure 4.7: DSC thermogram of CP7 laminate.

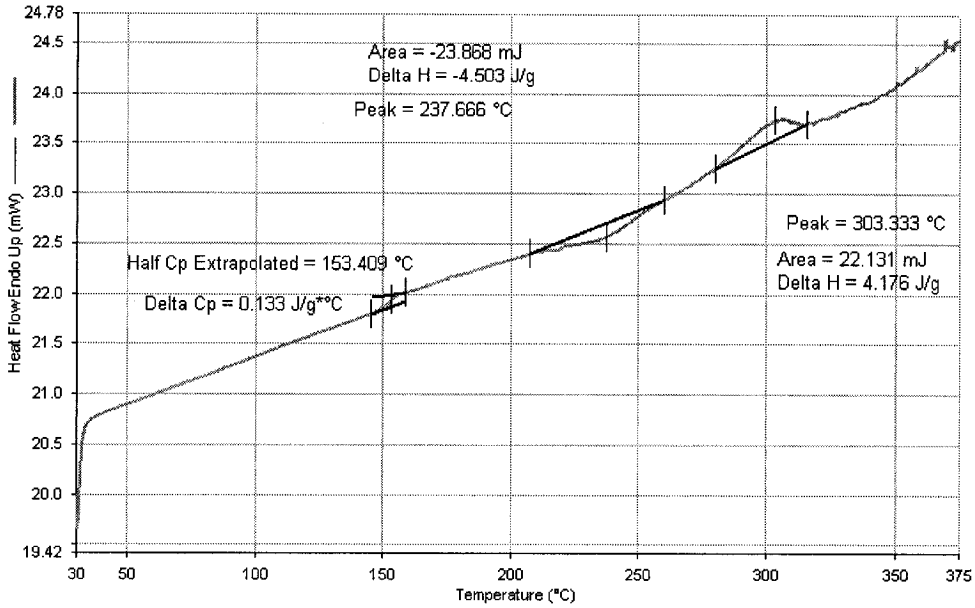


Figure 4.8: DSC thermogram of CP8 laminate.

The crystallinity results from repeating DSC experiments are listed in table 4.3.

Table 4.3: Crystallinity results from DSC analysis of the laminates.

Sample #	Test 1, % Crystallinity	Test 2, % Crystallinity	Average, % Crystallinity
CP1	17	15.7	16.3
CP2	15.7	13.1	14.4
CP3	13.1	12.6	12.8
CP4	12.9	10.7	11.8
CP5	10.7	10.5	10.6
CP6	8.8	10.3	9.5
CP7	7.5	8.8	8.1
CP8	6.6	8.8	7.7

The average crystallinity found in different specimens is illustrated in figure 4.9.

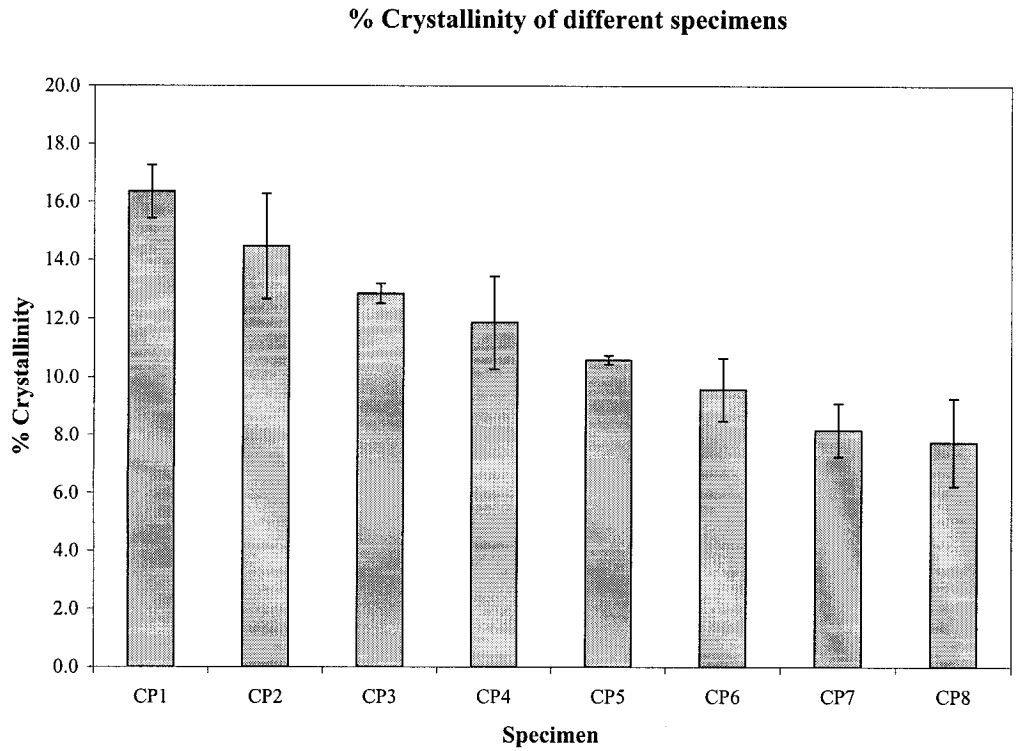


Figure 4.9: Average percent crystallinity found in 8 different laminates

4.2.3 Mechanical Properties

Since the variation in processing parameters affects the matrix properties, the mechanical properties of the laminates in matrix direction illustrate more variation when compared to the properties in the fiber direction.

Tables 4.4 and 4.5 list all the test results for transverse (90°) and axial (0°) laminates respectively.

Table 4.4: Transverse strength and Modulus of Carbon/PEKK laminates.

Sample #		Sample size		Max Load	Tensile Strength	Tensile Modulus
		W, mm	T, mm	N	MPa	GPa
CP1	1	24.07	1.03	1873.00	75.55	
	2	23.42	1.03	1726.55	71.57	
	3	23.79	1.00	1817.87	76.41	8.13
	4	24.49	0.99	1942.96	80.14	
	Mean	23.94	1.01	1840.10	75.92	
Standard Deviation		0.45	0.02	91.38	3.51	
CP2	1	24.84	1.02	1951.57	77.03	
	2	23.24	1.02	1734.21	73.16	
	3	25.10	1.03	1772.12	68.55	7.63
	4	23.75	1.03	1544.68	63.14	
	Mean	24.23	1.03	1750.65	70.47	
Standard Deviation		0.88	0.01	166.86	5.99	
CP3	1	24.43	1.03	1306.91	51.94	
	2	24.54	1.04	1692.86	66.33	
	3	24.47	1.02	1668.74	66.86	8.02
	4	23.51	1.02	1575.70	65.71	
	Mean	24.24	1.03	1561.05	62.71	
Standard Deviation		0.49	0.01	176.80	7.20	
CP4	1	23.45	1.02	1637.29	68.45	
	2	22.72	1.03	1469.47	62.79	
	3	24.29	1.00	1498.42	61.69	7.58
	4	25.28	1.05	1485.32	55.96	
	Mean	23.94	1.03	1522.63	62.22	
		1.10	0.02	77.35	5.12	
CP5	1	24.00	1.06	1137.28	44.70	
	2	24.13	1.06	1196.89	46.79	
	3	24.76	1.01	1466.72	58.65	7.37
	4	24.45	1.07	1439.84	55.04	
	Mean	24.34	1.05	1310.18	51.30	
Standard Deviation		0.34	0.03	167.38	6.63	
CP6	1	24.84	1.04	1237.56	47.91	
	2	23.79	1.03	1358.60	55.44	
	3	23.76	1.02	1217.31	50.23	10.48
	4	24.10	1.05	1565.36	61.86	
	Mean	24.12	1.04	1344.71	53.86	
Standard Deviation		0.50	0.01	159.78	6.20	
CP7	1	22.74	1.09	1453.28	58.63	
	2	23.56	1.02	1320.69	54.96	
	3	25.23	1.06	1592.93	59.56	7.64
	4	24.37	1.07	1093.25	41.93	
	Mean	23.98	1.06	1365.04	53.77	
Standard Deviation		1.07	0.03	212.57	8.14	

CP8	1	24.25	1.03	882.61	35.34	7.41
	2	24.58	1.03	1327.84	52.45	
	3	24.79	1.04	1193.10	46.28	
	4	24.17	1.04	1010.81	40.21	
	Mean	24.45	1.04	1103.59	43.57	
Standard Deviation		0.29	0.01	196.42	7.42	

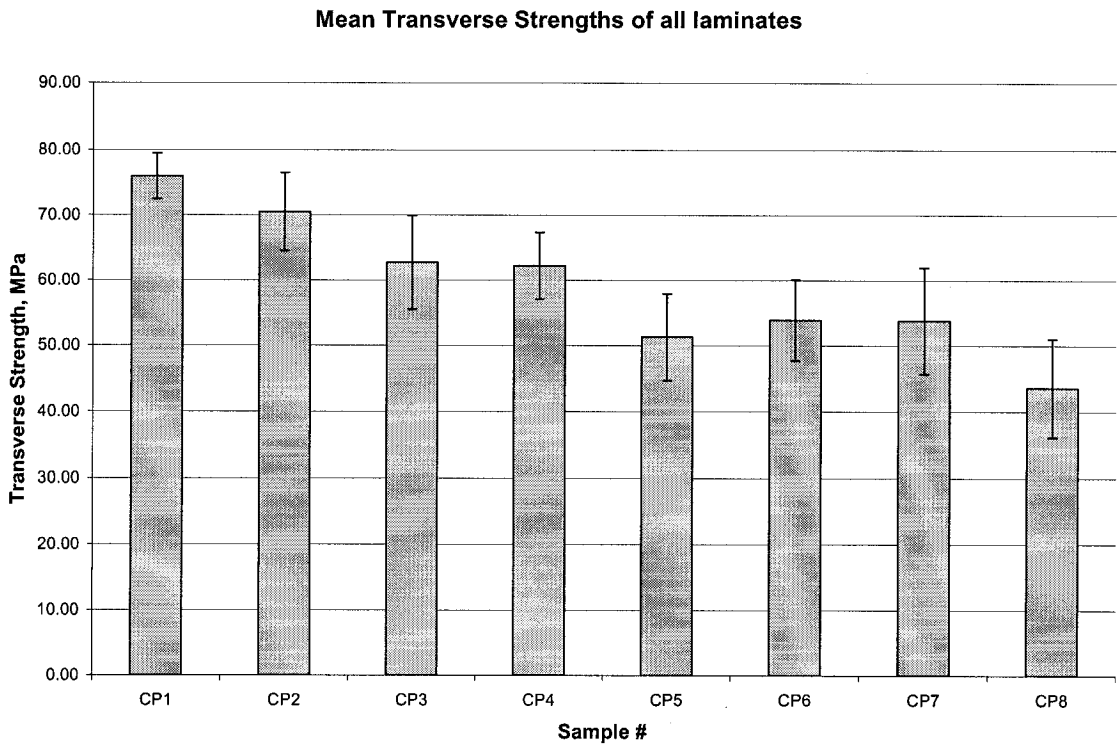


Figure 4.9a: Mean transverse strengths of all laminates.

Table 4.5: Axial strength and Modulus of Carbon/PEKK laminates.

Sample #		**Sample size**		**Max Load**	**Tensile Strength**	**Tensile Modulus**
		W, mm	T, mm	N	MPa	GPa
CP1	1	14.52	1.06	31366.60	2037.96	130.85
	2	13.15	1.04	28127.40	2056.70	
	3	12.33	1.05	26659.30	2059.19	
	4	13.87	0.99	29509.20	2149.05	
	5	13.01	1.00	25515.30	1961.21	

	Mean	13.38	1.03	28235.56	2052.82	
Standard Deviation		0.84	0.03	2308.77	66.95	
CP2	1	15.08	1.05	31463.10	1987.06	
	2	12.14	1.06	23840.50	1852.64	
	3	12.26	1.03	24691.70	1955.34	135.62
	4	11.67	1.00	22620.60	1938.35	
	5	13.92	1.04	28510.00	1969.36	
	Mean	13.01	1.04	26225.18	1940.55	
Standard Deviation		1.43	0.02	3663.59	52.31	
CP3	1	15.71	1.07	37114.60	2207.93	
	2	13.05	1.06	27731.10	2004.71	
	3	12.53	1.06	25977.00	1955.83	137.16
	4	12.63	0.99	24671.00	1973.10	
	5	13.86	0.98	26418.10	1944.97	
	Mean	13.56	1.03	28382.36	2017.31	
Standard Deviation		1.31	0.04	5002.36	108.93	
CP4	1	14.77	1.13	31859.40	1908.88	
	2	13.26	1.10	26921.20	1845.69	
	3	13.49	1.08	27252.10	1870.53	133.33
	4	13.53	1.04	25374.00	1803.26	
	5	12.50	1.00	23278.80	1862.30	
	Mean	13.51	1.07	26937.10	1858.13	
Standard Deviation		0.82	0.05	3168.40	38.45	
CP5	1	11.94	1.05	20201.50	1611.35	
	2	10.68	1.07	24333.30	2129.34	
	3	10.78	1.05	23875.00	2109.29	134.15
	4	10.97	1.05	21142.30	1835.51	
	5	11.52	1.02	22451.70	1910.72	
	Mean	11.18	1.05	22400.76	1919.24	
Standard Deviation		0.54	0.02	1755.79	213.39	
CP6	1	13.66	1.08	28182.50	1910.32	
	2	12.26	1.08	24378.10	1841.13	
	3	12.30	1.02	24678.00	1967.00	133.59
	4	11.73	1.00	23785.40	2027.74	
	5	12.33	1.00	21976.20	1782.34	
	Mean	12.46	1.04	24600.04	1905.71	
Standard Deviation		0.72	0.04	2260.39	97.55	
CP7	1	11.92	1.09	23702.70	1824.29	
	2	11.54	1.06	23220.20	1898.25	
	3	11.81	1.01	22534.40	1889.19	122.00
	4	11.70	1.00	23044.50	1969.62	
	5	11.20	0.99	20890.70	1884.08	
	Mean	11.63	1.03	22678.50	1893.09	
Standard Deviation		0.28	0.04	1083.21	51.75	
CP8	1	13.70	1.08	26249.30	1774.08	
	2	13.63	1.05	26197.60	1830.53	
	3	11.44	1.08	21287.00	1722.92	123.75

	4	12.31	1.01	22131.30	1780.03	
	5	13.04	1.06	26059.70	1885.32	
	Mean	12.82	1.06	24384.98	1798.58	
Standard Deviation		0.95	0.03	2461.83	61.67	

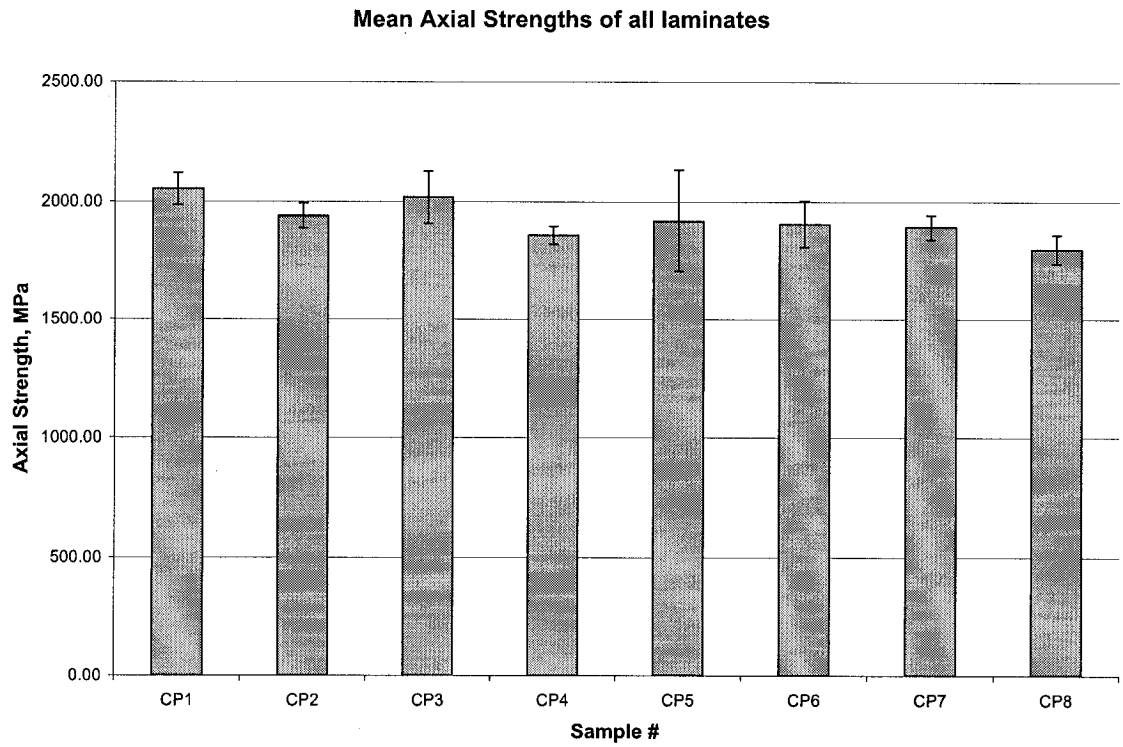
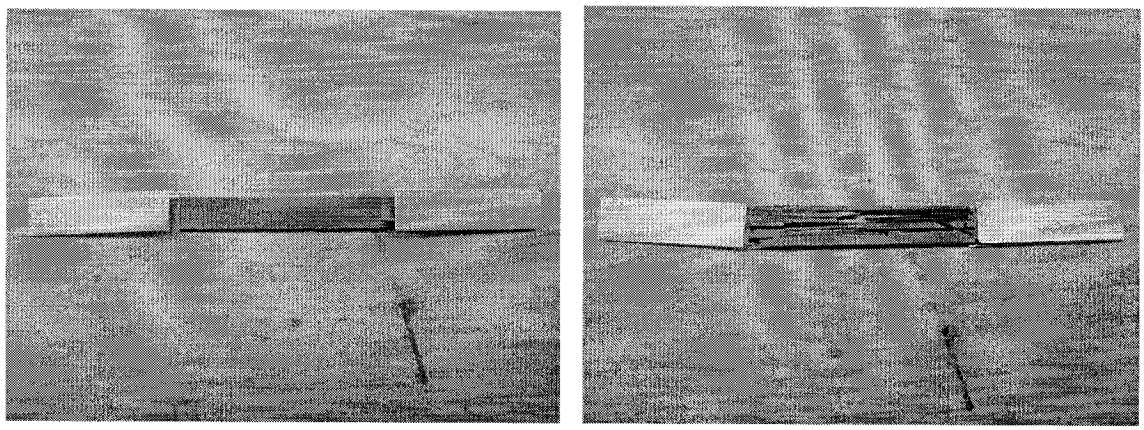


Figure 4.9b: Mean axial strengths of all laminates.

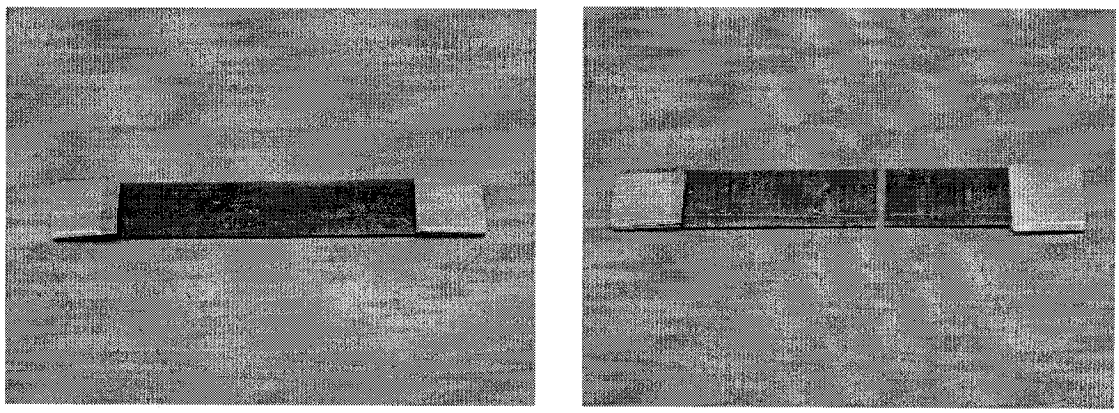
Among all the test results obtained from both axial and transverse laminates, the maximum tensile strength and modulus in axial direction are 2130 MPa and 161 GPa respectively. For transverse direction they are 80 MPa and 10.5 GPa.

The failure of the specimens is shown in figures 4.10 (axial specimens) and 4.11 (transverse specimens).



(a) before (b) after

Figure 4.10: Typical failure of axial (0°) specimen (a) before and (b) after tensile testing.



(a) before (b) after

Figure 4.11: Typical failure of transverse (90°) specimen (a) before and (b) after tensile testing.

Axial and transverse failure mechanisms for all the eight sets of laminates are illustrated in figures 4.12 and 4.13. One sample from each set of the laminates is shown for both axial and transverse directions to comprehend the failure pattern. The samples are arranged from left to right in an order of CP1 to CP8.

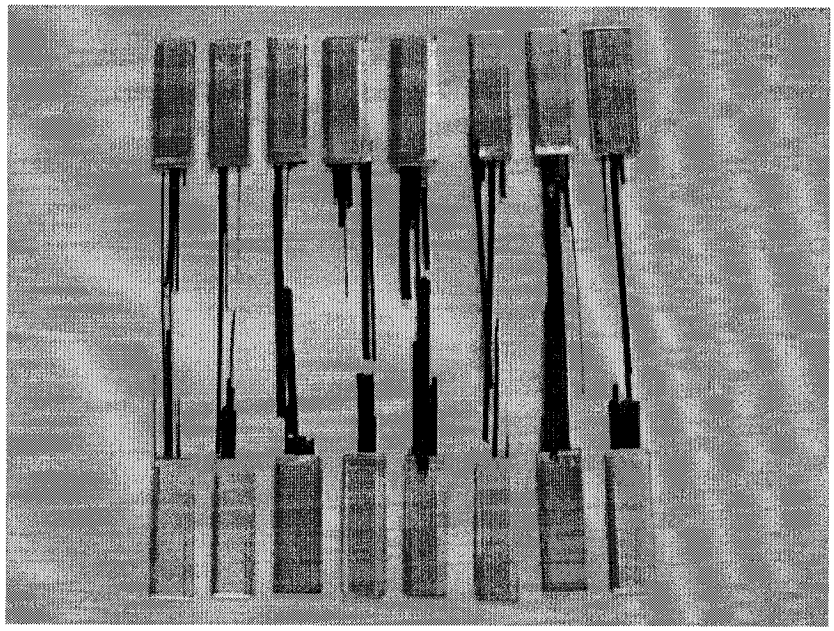


Figure 4.12: Failure of axial samples (CP1 to CP8)

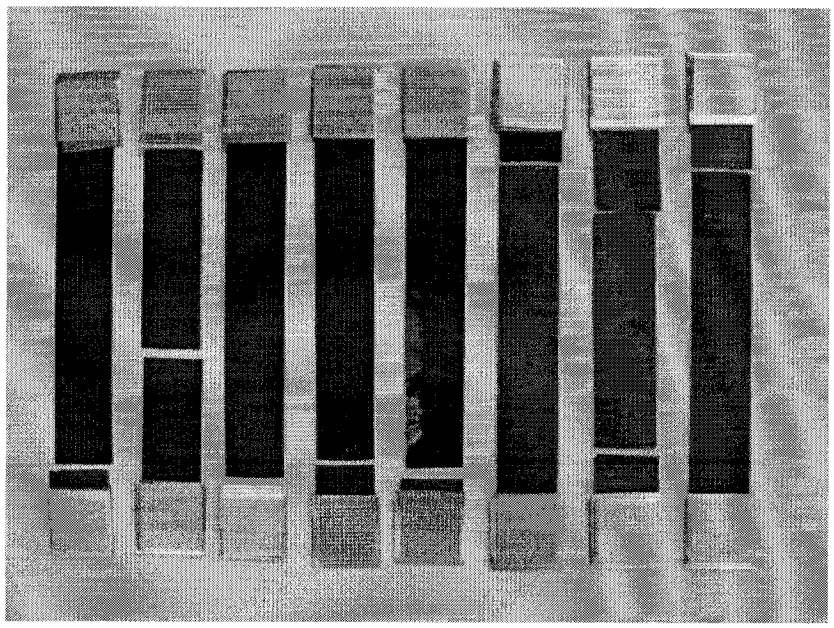


Figure 4.13: Transverse failure of samples (CP1 to CP8).

The failure begins with the resin cracking followed by fiber breakage for the axial specimens. In contrast, for the transverse specimens, failure occurs because of the fracture in the resin which initiates from the fiber resin interface.

The summary of the properties (average value) obtained for both axial and transverse laminates are shown in table 4.6 with respect to crystallinity.

Table 4.6: Percent Crystallinity and Average Tensile properties of 0° and 90° laminates.

Sample #	Tensile Strength, MPa		Tensile Modulus, GPa		% Crystallinity
	Axial (0)	Transverse (90)	Axial (0)	Transverse (90)	
CP1	2052.8	75.9	130.8	8.1	16.3
CP2	1940.5	70.4	135.6	7.6	14.4
CP3	2017.3	62.7	137.1	8.0	12.8
CP4	1858.1	62.2	133.3	7.6	11.8
CP5	1919.2	51.3	134.1	7.4	10.6
CP6	1905.7	53.8	133.6	10.5	9.5
CP7	1893.0	53.7	122.0	7.6	8.1
CP8	1798.5	43.5	123.7	7.4	7.7

The average mechanical properties (table 4.6) obtained from this research resemble those obtained by the researchers [19,42] using Carbon/PEKK tape prepreg laminates. This assures that the integrity of the present work is acceptable

Figures 4.14 and 4.15 describe the effects of crystallinity on the strengths of the laminates. In figure 4.14, the data points are more in the vicinity of the trend line than in figure 4.15. Also, the points in figure 4.14 have more tendencies to conform to the decreasing transverse strengths with the decreasing crystallinity than the ones in figure 4.15. Also the slope of the transverse strength line is more than that of the axial strength line. This indicates that the polymer crystallinity is more dominant for the transverse

properties than the axial ones. The maximum transverse strength was found in CP1 laminate for the maximum amount of crystallinity. It is noteworthy that the variation in crystallinity in the laminates is due to the variation in cooling rate. In this work, the cooling rate was within a range of 7 - 10°C/min and the crystallinity varied from 7 to 16%. The transverse strength of the laminates varied from 45 MPa to 75 MPa. This shows that the variation in cooling rate can have a significant effect on the final properties of the laminates. The discrepancy in crystallinity with respect to respective cooling rates and their relation have not been studied in this work. This has been recommended as one of the future works.

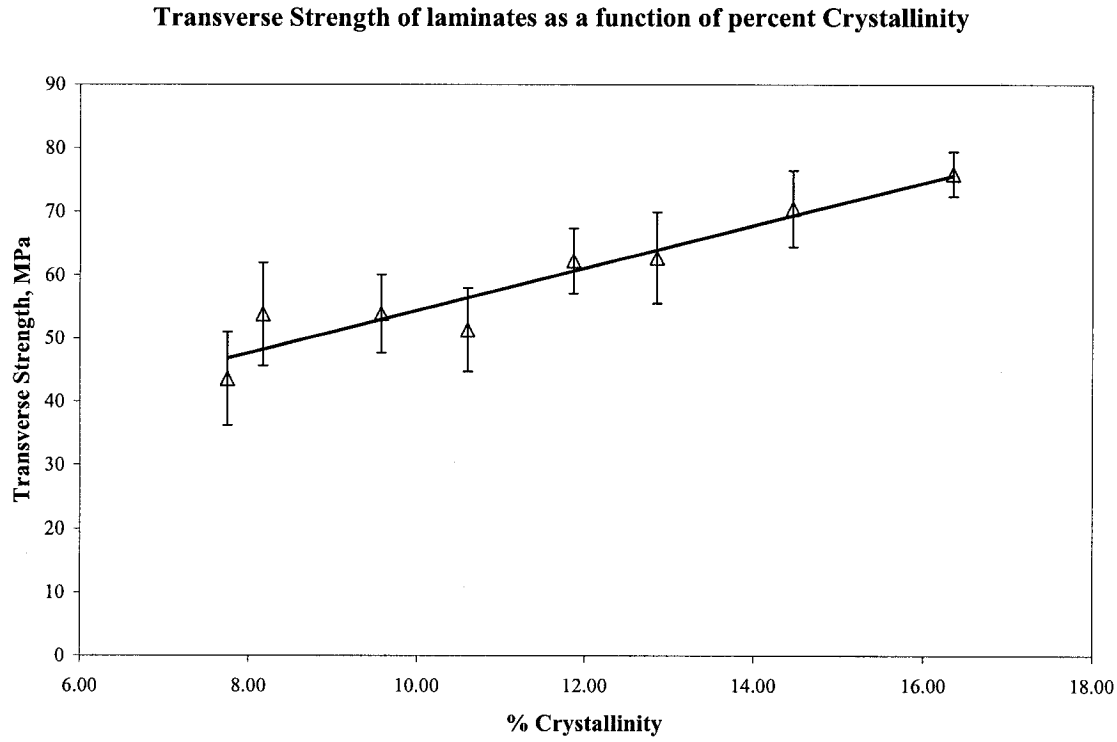


Figure 4.14: Variation of Transverse Strength of laminates with percent crystallinity.

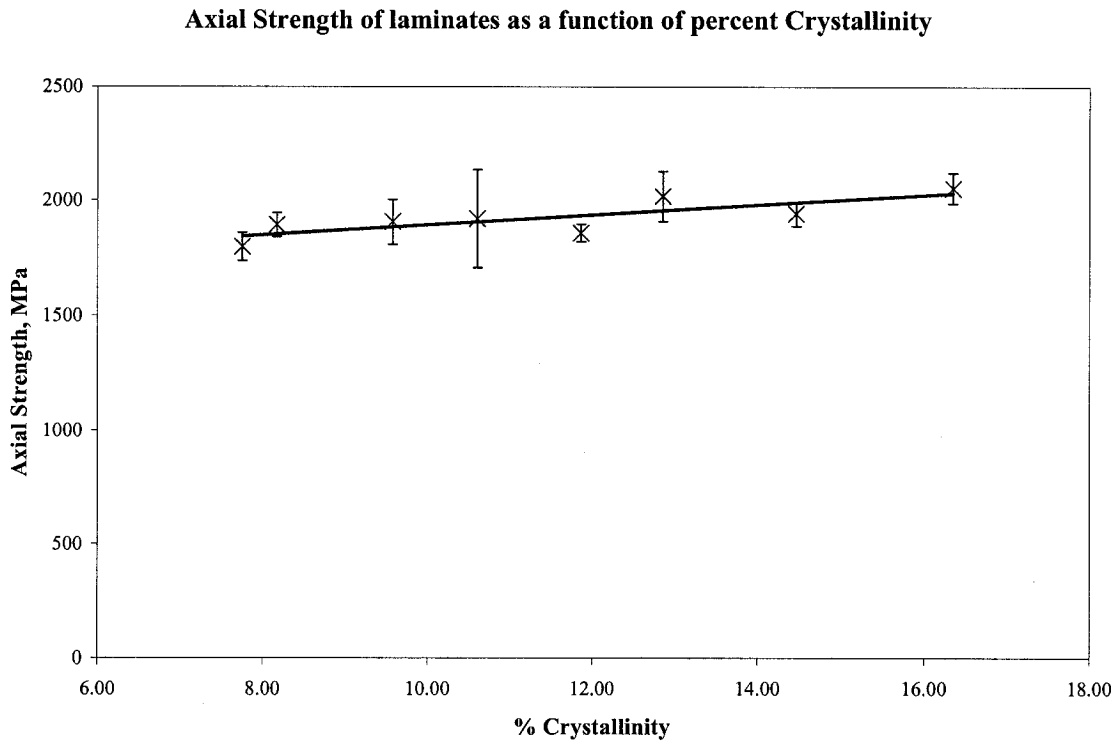


Figure 4.15: Variation of Axial Strength of laminates with percent crystallinity.

4.3 Observations

The results obtained are compared pair by pair in this section. Two sets of parameters with only one variable among them are compared and their corresponding results are discussed.

The complete processing and testing cycle is divided into a few major stages. Every single stage is significant and provides feedback to the initial parameters so that a better quality laminate can be obtained. It works like a closed loop system. Figure 4.16 explains the whole cycle by a simple block diagram.

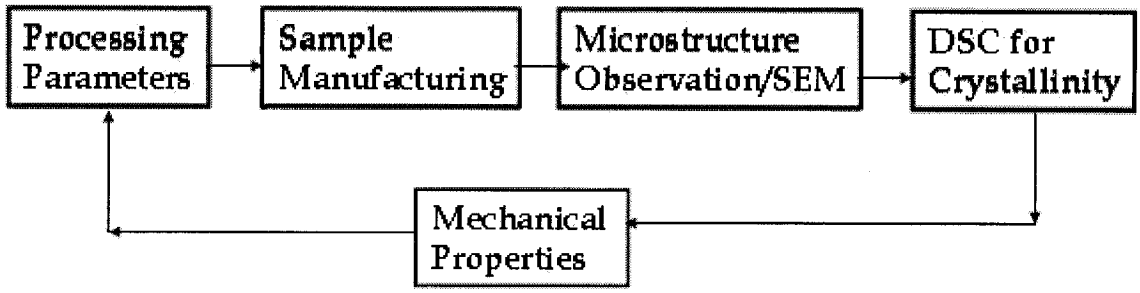


Figure 4.16: Block diagram of the complete processing and testing cycle of the laminates.

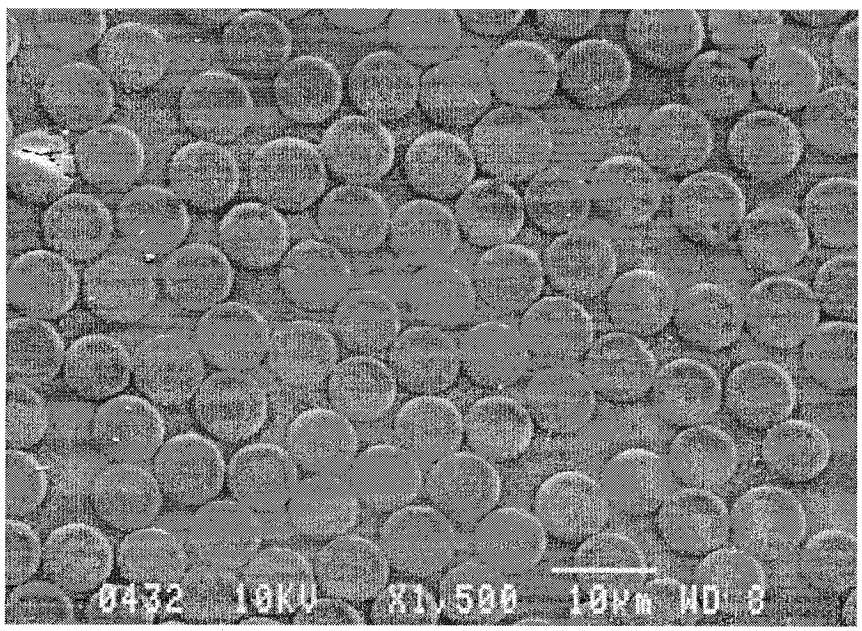
The results those are presented in this chapter are the best results achieved after being improved from similar experiments conducted at a prior stage of this research. The processing parameters have been improved by the feedback provided by each stage of the whole process as mentioned in figure 4.16. For example, in some prior experiments, the consolidation parameters used were similar except there was no solidification pressure applied and the dwell time was 5 minutes in some cases. More void contents were observed during microstructural study and the mechanical property results did not show acceptable values as found by other researchers [19, 42]. Namely, axial strengths found were within a range of 1380 to 1800 MPa. Even greater amount of fiber disorientation and waviness were observed when a pressure of 2.75 MPa (400 psi) was used as consolidation pressure. These mediocre results insisted in understanding the shortcomings of the laminate quality and helped in determining better processing parameters to obtain improved consolidation quality and subsequently superior mechanical properties.

From all the experiment results presented in this chapter, the tensile strengths and moduli obtained in the axial direction are within the range of 1800 to 2050 MPa and 122 to 137

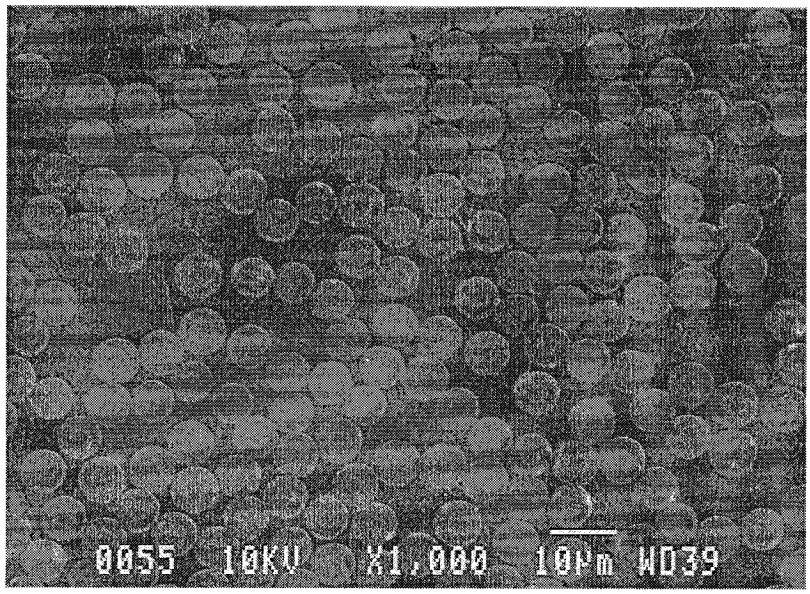
GPa respectively. These values show that within the processing window used in this research, the axial properties do not vary significantly. Conversely, the transverse direction properties show a larger range of variation within a smaller amount of absolute values. The latter confirms that variation in consolidation parameters and cooling rates changes the fiber matrix adhesion, amount of void content, fiber matrix distribution, matrix morphology and eventually the mechanical properties in the matrix direction.

4.3.1 Effect of Temperature Change

Referring to table 4.1, laminate CP1 and CP2 have similar consolidation parameters except temperature. When observed, the microstructure revealed void free fiber matrix distribution for both the laminates.



(a)



(b)

Figure 4.17: Cross-section of (a) CP1 laminate consolidated using parameters of 1.72 MPa, 15 min and 345°C; (b) CP2 laminate consolidated using parameters of 1.72 MPa, 15 min and 325°C.

Transverse and axial stress vs. strain curves for these two laminates are compared below in figures 4.18 and 4.19 respectively.

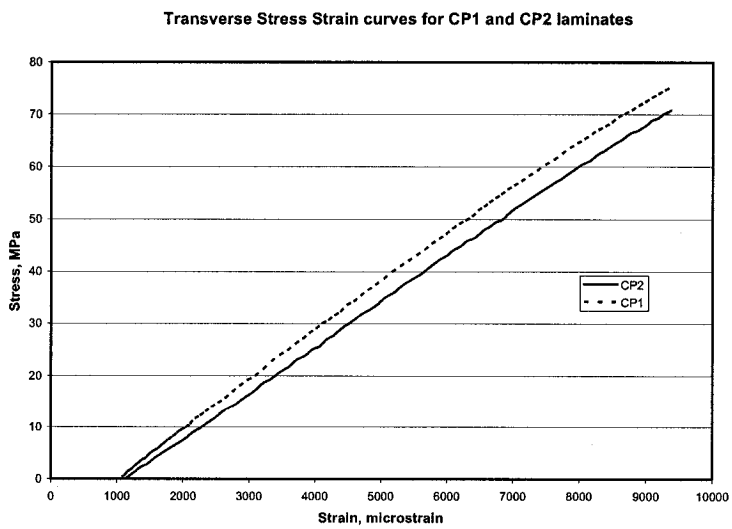


Figure 4.18: Transverse Stress vs. Strain curves for CP1 and CP2 laminates.

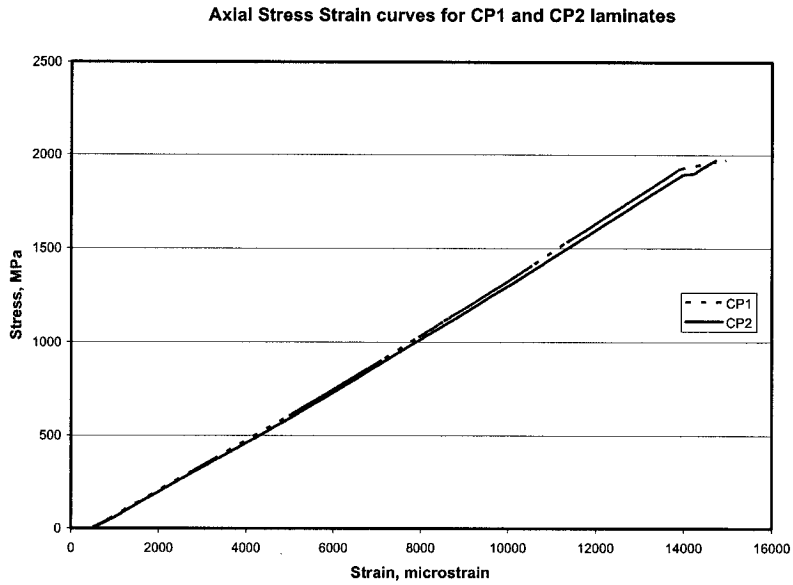
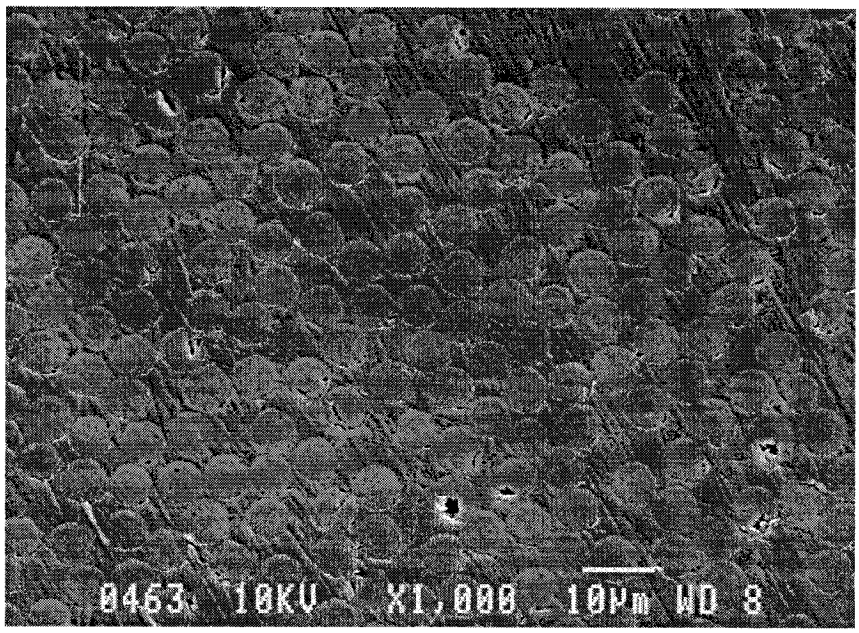


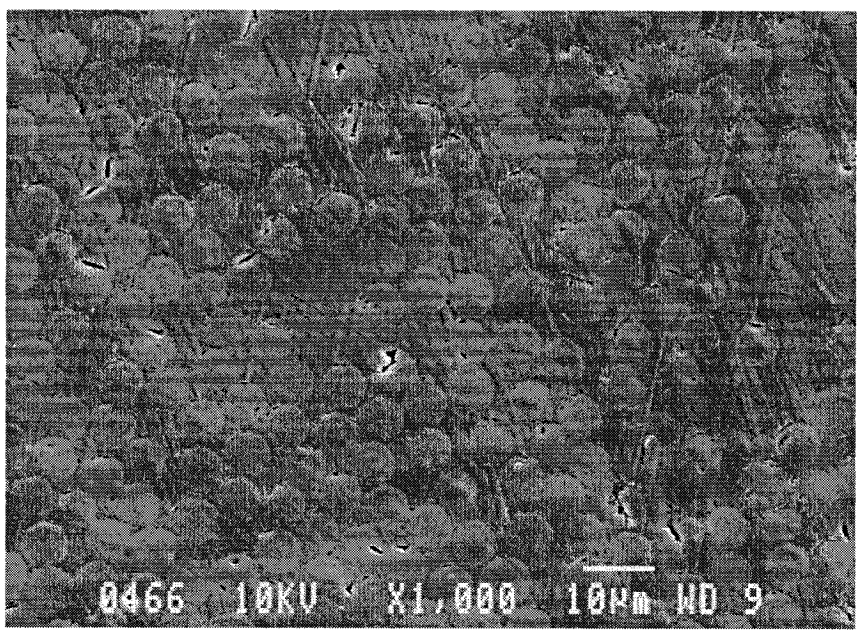
Figure 4.19: Axial Stress vs. Strain curves for CP1 and CP2 laminates.

The little variation in transverse mechanical properties of these two laminates is attributed to the difference in their crystallinity which is 16.3% and 14.4% respectively (table 4.3). The properties for CP1 and CP2 laminates are superior since the pressure and time are high enough to suppress the voids and allows the resin to flow and provide better fiber distribution throughout the laminate.

Similarly, the temperature difference does not show much variation when the cross sections are observed for other laminates. It is evident in the laminates CP7 and CP8 where temperature was the only variable among all the parameters and is shown in figure 4.20.



(a)



(b)

Figure 4.20: Cross-section of (a) CP7 laminate consolidated using parameters of 1.38MPa, 10 min and 345°C; (b) CP8 laminate consolidated using parameters of 1.38MPa, 10 min and 325°C.

Both the cross sections in figure 4.20 have voids in them and this can be attributed to the lower consolidation pressure and time. The pressure and time was not high enough to suppress the voids and make an even distribution of fibers in the matrix. This supports the results obtained from CP1 and CP2 laminates where the pressure and time were 1.72 MPa and 15 minutes respectively.

The transverse and axial stress vs. strain curves for CP7 and CP8 laminates are presented in figures 4.21 and 4.22 respectively.

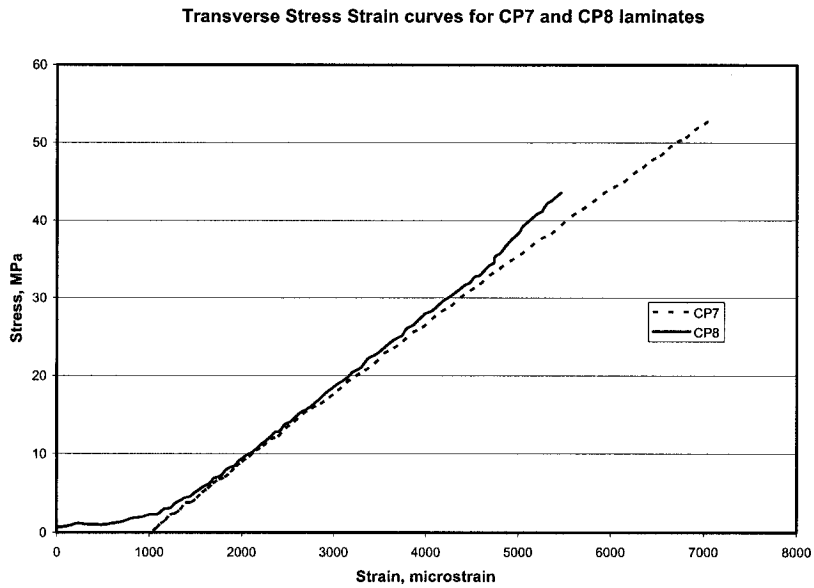


Figure 4.21: Transverse Stress vs. Strain curves for CP7 and CP8 laminates.

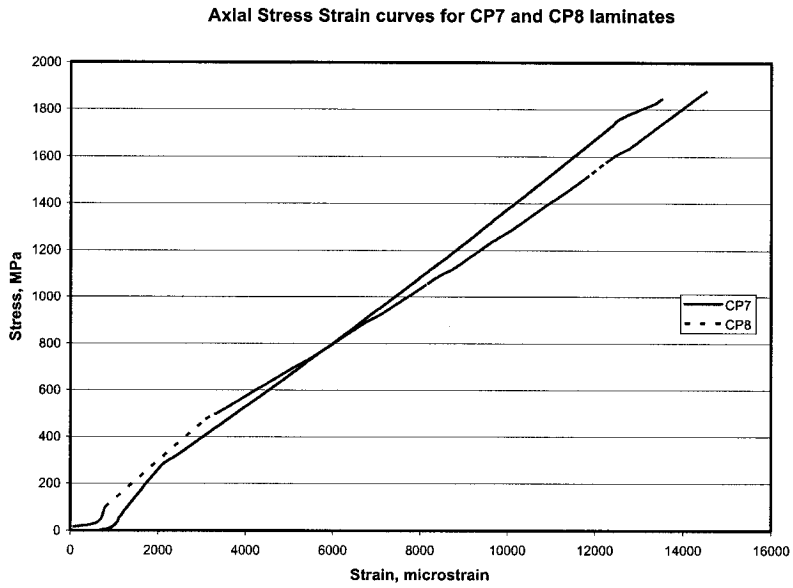


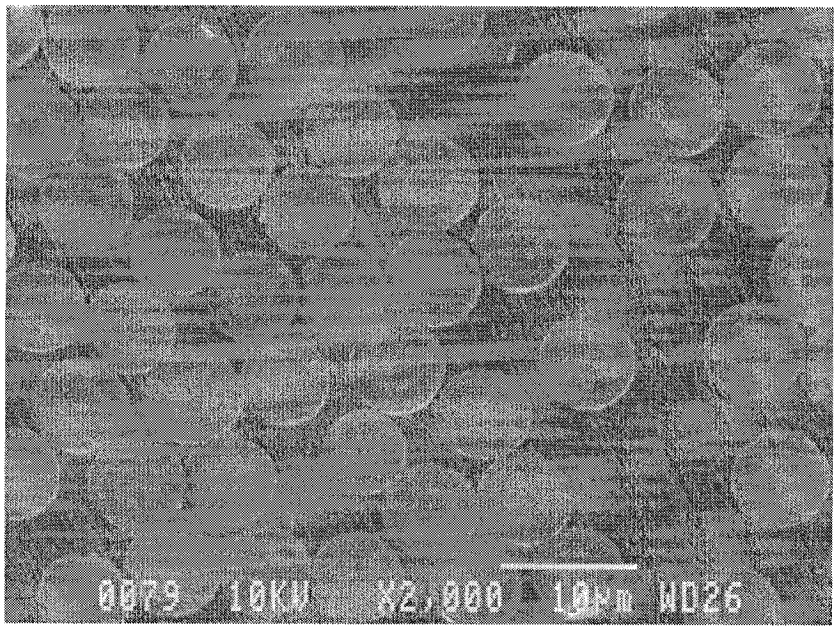
Figure 4.22: Axial Stress vs. Strain curves for CP7 and CP8 laminates.

The difference in transverse strength of CP7 and CP8 laminates are due to the difference in their respective crystallinity (table 4.3).

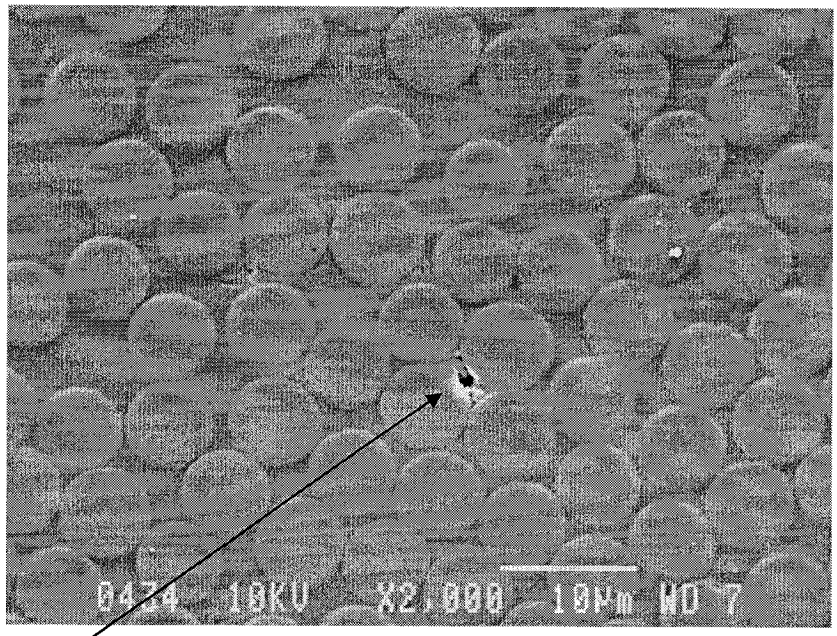
The processing range of temperature for PEKK, found in literatures [19,42], is from 315°C to 370°C. The two different temperatures, 325°C and 345°C, used in this work, falls within this range and do not show any polymer degradation during consolidation. Hence the temperatures adapted in this work are not a major factor to consider when compared to other parameters. For tape prepreg consolidation, the employed variation in temperature within the moderate processing range will not affect the final properties of the laminates.

4.3.2. Effect of Pressure Change

Laminate CP2 and CP3 have identical processing parameters except the pressure. The pressure applied during consolidation and cooling is higher in CP2 than in CP3. The decrease in pressure in CP3 laminate reveals presence of voids which is presented in figure 4.23.



(a)



(b)

Figure 4.23: Cross-section of (a) CP2 laminate consolidated using parameters of 1.72MPa, 15 min and 325°C; (b) CP3 laminate consolidated using parameters of 1.38MPa, 15 min and 325°C.

The application of higher pressure during consolidation and subsequently during cooling cycle helps to suppress the nucleation of voids [59]. This phenomenon is evident in figure 4.23 where presence of void is visible in CP3 laminate. Pressure is the only parameter which is different between these two laminates. Because of the presence of voids, the subsequent transverse strength of CP3 laminate (figure 4.24) is lower than CP2 laminate. Axial strength of the laminates (figure 4.25) is not much affected by the matrix defect such as void. Also the higher transverse strength of CP2 laminate over CP3 can be described in terms of higher percentage of crystallinity (table 4.3).

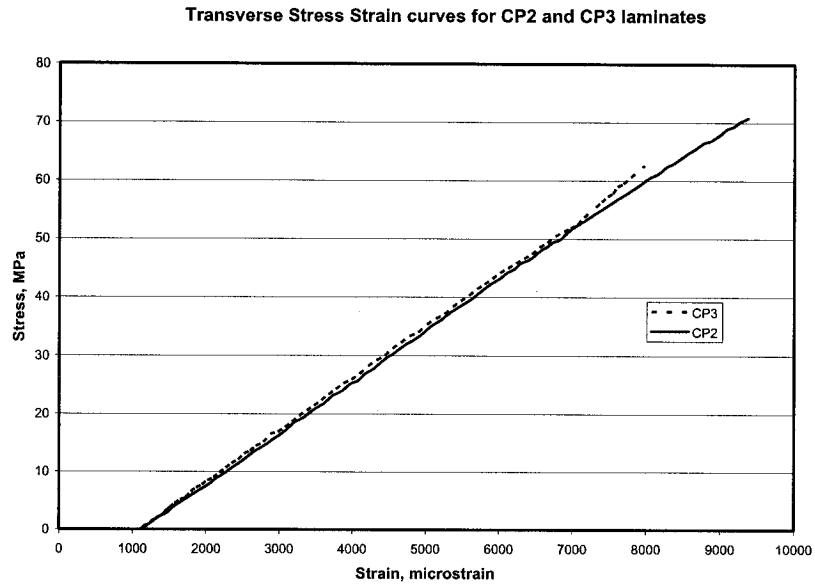


Figure 4.24: Transverse Stress vs. Strain curves for CP2 and CP3 laminates.

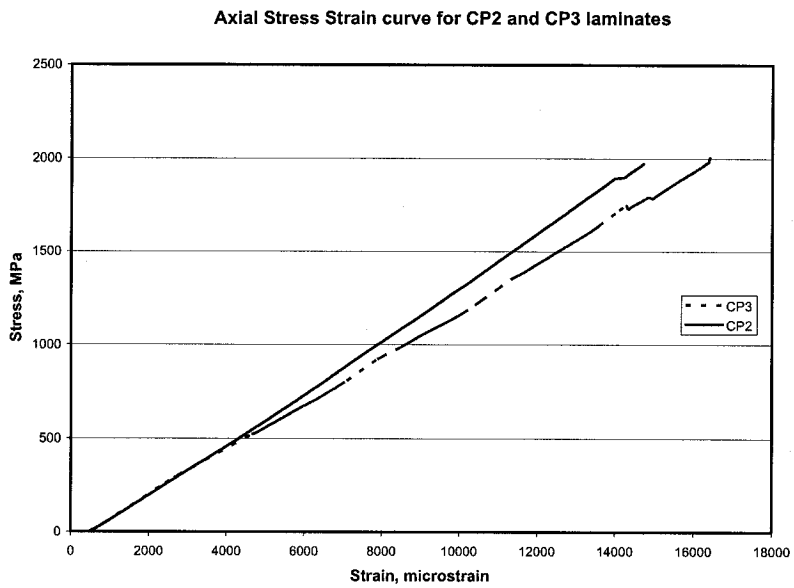
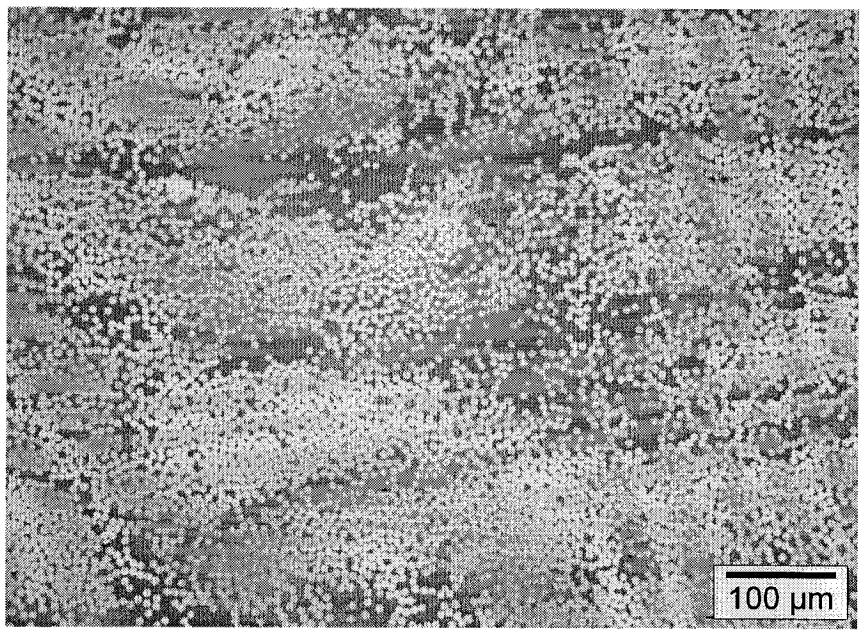


Figure 4.25: Axial Stress vs. Strain curves for CP2 and CP3 laminates.

Likewise, CP5 and CP8 laminates also confirm the effect of lower pressure on the microstructure. Figure 4.26 shows the difference in microstructure in terms of variation in pressure. Both the laminates have identical parameters except for pressure. But the

consolidation time is 10 minutes which is different than CP2 and CP3 laminates. Barnes and Cogswell [54] mentioned about formation of a resin rich interlayer between prepreg plies under a pressure of 1.01 MPa (~145 psi) during consolidation. Resin rich areas between ply interfaces are noticed in figure 4.26 for both CP5 and CP8 laminates. Moreover, void contents are evident in CP8 laminate and are contributed to the lower consolidation and cooling pressure when compared to laminates with higher properties.



(a)

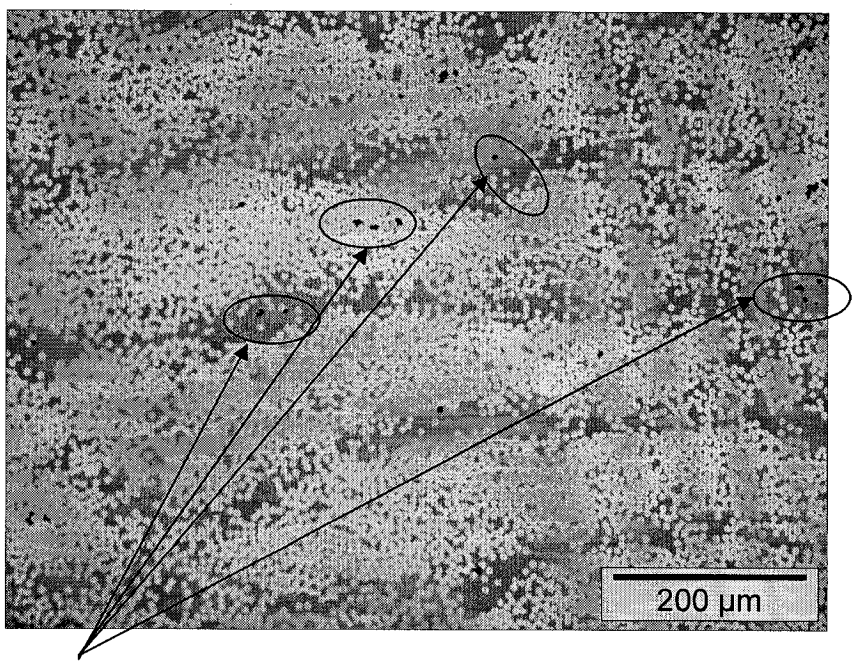


Figure 4.26: Cross-section of (a) CP5 laminate consolidated using parameters of 1.72MPa, 10 min and 325°C; (b) CP8 laminate consolidated using parameters of 1.38MPa, 10 min and 325°C.

The transverse and axial strengths of CP5 and CP8 laminates are shown in figures 4.27 and 4.28 respectively.

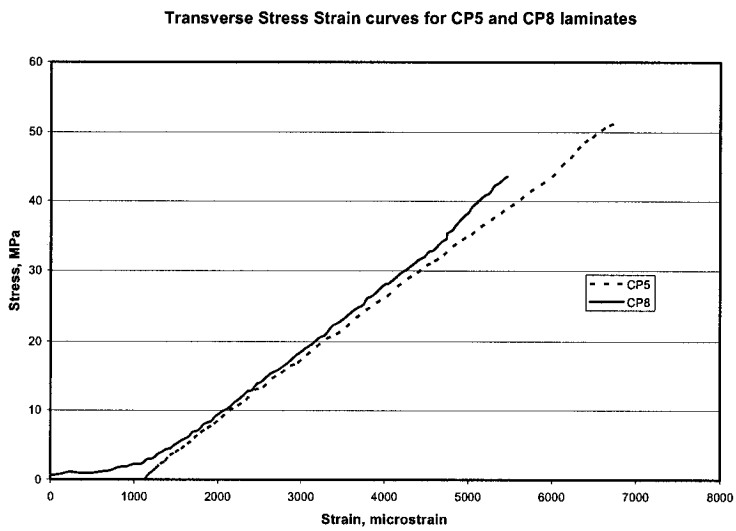


Figure 4.27: Transverse Stress vs. Strain curves for CP5 and CP8 laminates.

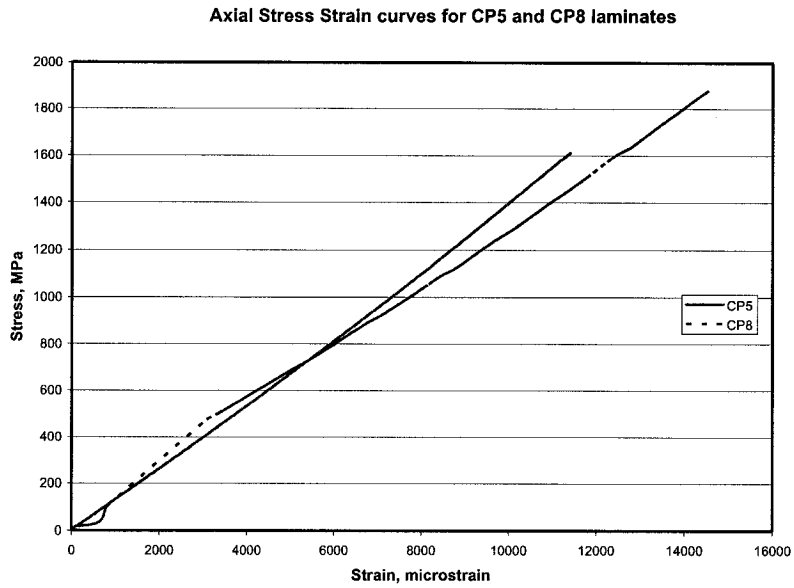


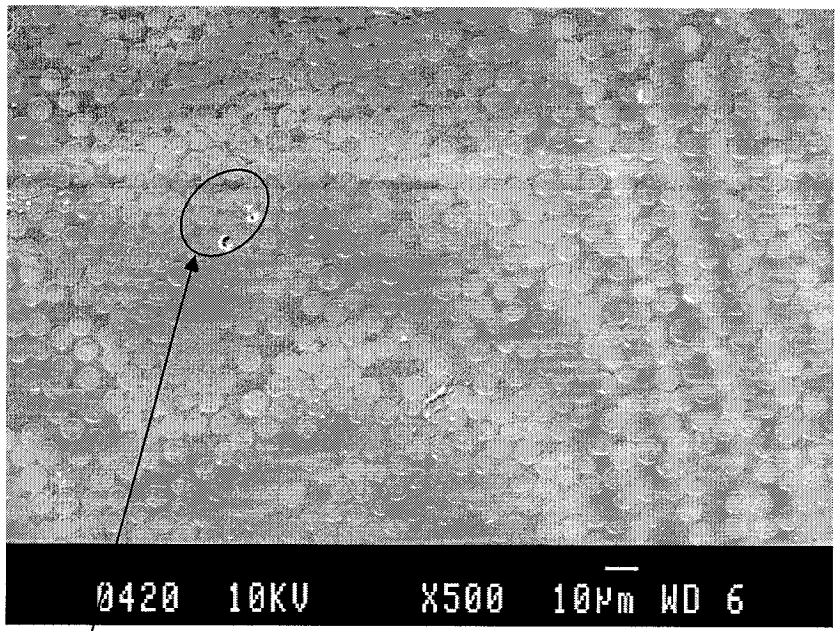
Figure 4.28: Axial Stress vs. Strain curves for CP5 and CP8 laminates.

Presence of significant amount of voids in CP8 laminate eventually produced lower transverse strength than CP5 laminate (figure 4.27). Also the amount of crystallinity varies from 10.6% (CP5) to 7.7% (CP8) (table 4.3).

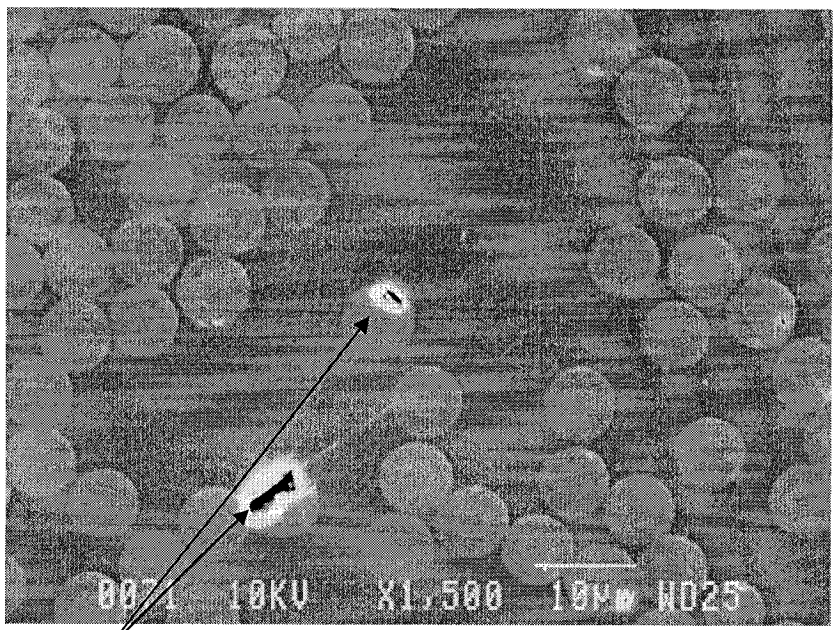
As the results show, pressure is one of the major factors to be considered as a consolidation parameter for tape prepreg laminate manufacturing and to obtain useful laminate properties when combined with other efficient selection of parameters.

4.3.3 Effect of change in consolidation time

Sufficient consolidation time is required to allow the resin to flow at the consolidation temperature and to perfectly wet the fibers to avoid any dry region inside the laminate. Under sufficient pressure, it also makes sure that coalesce ace of multi layers inside the laminate has occurred and the excess resin is flushed out. The effect of change in time as a consolidation parameter is illustrated in figure 4.29 by comparing the microstructures of CP4 and CP7 laminates and is subsequently discussed.



Voids (a)



Voids (b)

Figure 4.29: Cross-section of (a) CP4 laminate consolidated using parameters of 1.38 MPa, 15 min and 345°C; (b) CP7 laminate consolidated using parameters of 1.38 MPa, 10 min and 345°C.

From figure 4.29a, it is obvious that CP4 exhibits presence of voids as the consolidation pressure is lower (1.38 MPa) but it has a better fiber matrix distribution, hence good compaction of fibers because of 15 minutes of consolidation time. On the other hand, in figure 4.29b, CP7 laminate illustrates voids as well as resin rich regions which can be contributed to both lower pressure (1.38 MPa) and 10 minutes of consolidation time.

The transverse and axial strengths of these laminates are presented in figures 4.30 and 4.31 respectively.

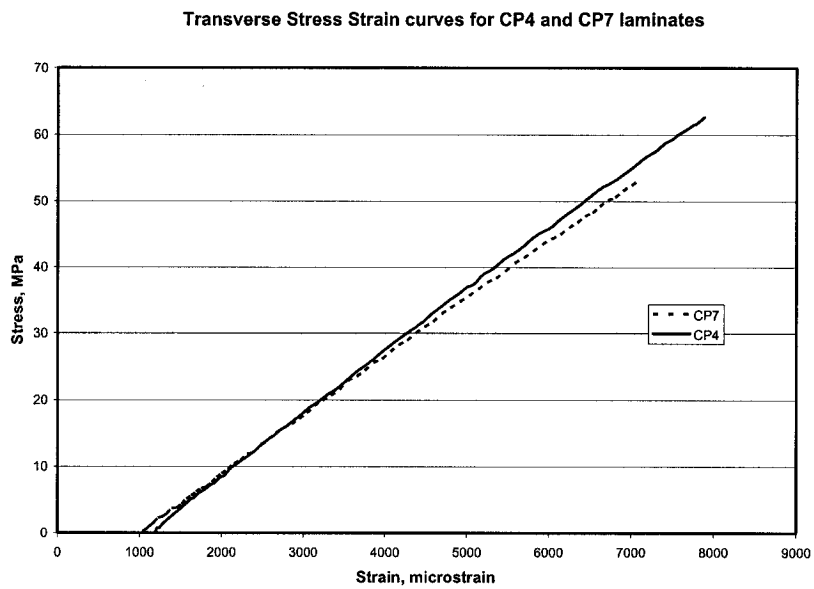


Figure 4.30: Transverse Stress vs. Strain curves for CP4 and CP7 laminates.

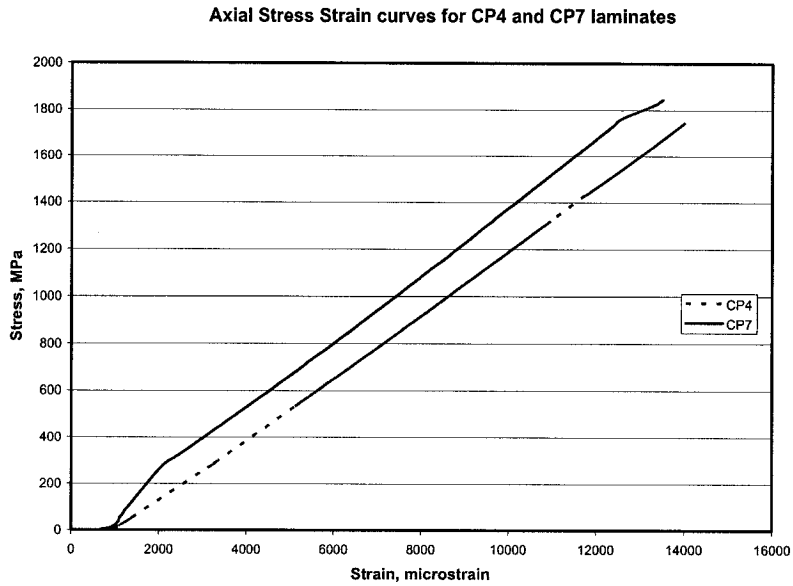


Figure 4.31: Axial Stress vs. Strain curves for CP4 and CP7 laminates.

From the figure it is noticeable that transverse strength of CP4 laminate is way higher than CP7. This also confirms the crystallinity results (CP4 - 11.8% and CP7 – 8.1%) obtained for these two laminates (table 4.3).

4.3.4 Optimum processing window

From the results achieved, a difference in the mechanical properties in accordance with the consolidation parameters can be interpreted to specify the optimum processing window for Carbon/PEKK thermoplastic composites. The results can be categorized in two different sets: a) higher end results, b) lower end results.

Taking the case of transverse strength, which is mostly affected by the variation in processing parameters, higher end results include the range from 60 to 75 MPa (table 4.6), whereas lower end results incorporate the range from 43 to 59 MPa (table 4.6). The

higher end results are obtained by using 15 minutes of consolidation time and pressures of 1.72 and 1.38 MPa. Even within the higher range, the laminates consolidated under 15 min and 1.72 MPa pressure show a little better properties than those of 15 minutes and 1.38 MPa of pressure. This implies that the increase in pressure at the final stage of processing has helped in removing the voids to a considerable extent hence increased the mechanical properties.

The lower end results are obtained from parameters where the consolidation time is 10 minutes, which is not sufficient to distribute the fibers evenly by squeezing the extra resin out of the system to provide a void free laminate. Figure 4.32 depicts the overall comparison of these two categories of results in terms of transverse strength of the laminates.

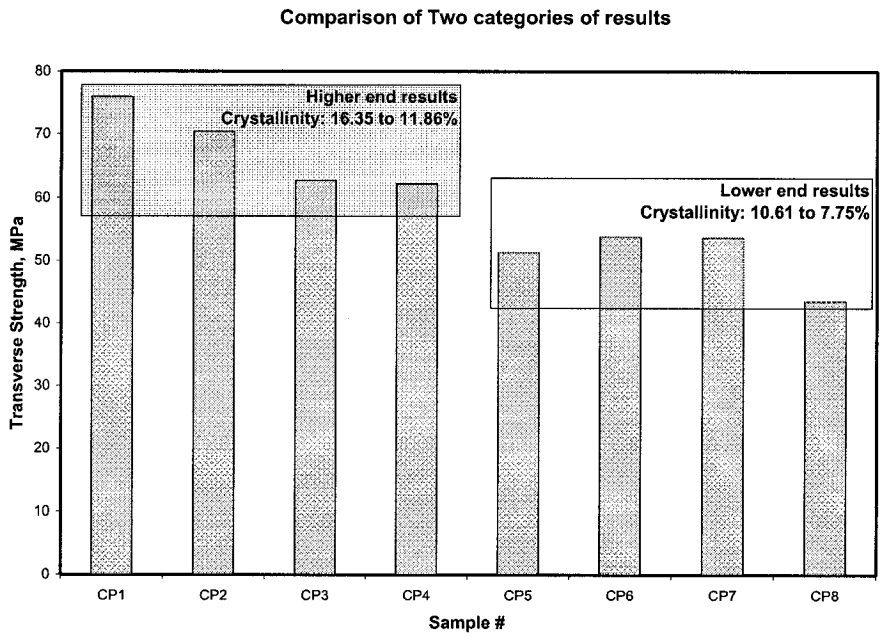


Figure 4.32: Comparison to two categories of results obtained from all the experiments.

The increase in consolidation time from 10 to 15 minutes has augmented the fiber volume fraction by flushing the excess resin out of the laminate, hence providing void free compacted fiber bundles and eventually improving the mechanical properties.

In accordance with the results and discussions, an optimum processing window can be suggested from the set of processing parameters used in this research. All higher end results were obtained from the parameters where the consolidation time was 15 minutes, which can be considered as a primary variable for better quality laminates. Also, as a secondary variable, a higher pressure of 1.72 MPa used over that range played a role in developing good laminate properties, compared to the ones where 1.38 MPa of pressure has been used. The lower end results can all be attributed to the 10 minutes of consolidation time. Even within the lower end results, 1.72 MPa of pressure yields improved mechanical properties which conform to the explanation mentioned above for higher end results.

4.4 Conclusion

Adopted consolidation parameters to determine the effects of those on the final properties of the laminates are presented. Effects of processing parameters on the consolidation quality of the laminates have been evaluated by presenting and verifying the results of microstructural observation, percent crystallinity and mechanical property. Finally observations from the results are put forward to summarize the contribution of the work.

CHAPTER 5

CONCLUSIONS, CONTRIBUTION AND RECOMMENDATIONS

5.1 Conclusions

There is considerable interest in advanced thermoplastic composites in the high performance application industries. Already, an interesting choice of these materials is available in the marketplace for use as matrices for composites in applications like aircraft structures.

In general, thermoplastic resins exhibit mechanical properties comparable to those of thermosets but they are characterized by outstanding high toughness, higher ductility and lower moisture absorption. They demonstrate good temperature capability as they possess high glass transition temperature (T_g). But the very high T_g leads to high melt viscosity which renders the complete impregnation of the fibers by the matrix difficult and thus impeding the availability of some thermoplastic resins in the prepreg form.

There are major benefits in processing thermoplastic composites compared to thermoset composites including the unlimited shelf life, short processing cycles and the ability to be remelted and reprocessed. The main drawbacks are high melt viscosity, high processing temperature and the lack of tack and drape of most prepregs.

In the present work, an elaborate discussion in understanding the behavior of the material during processing and various challenges to overcome was presented. Upon realizing the importance of the processing parameters, the material for the research work was selected and the parameters to fabricate the laminates are defined. Using compression molding technology, the laminates are manufactured from unidirectional prepreg tape under different processing conditions and evaluated for their structural integrity. The evaluation of the consolidation quality is performed in a few steps; by investigating the microstructure, the crystallinity of polymer and primary tensile properties in both fiber and matrix directions.

5.2 Contribution

An investigation on the effects of processing parameters on the mechanical properties of Carbon/PEKK thermoplastic composites was performed. Consolidation quality of laminates was improved by varying the parameters and verifying the corresponding results obtained from the steps mentioned in the previous section. Interpretation of the results eventually established an association of various parameters with the final properties of the laminates. Excellent mechanical properties are obtained employing consolidation parameters with higher time and pressure with moderate processing temperature. A processing window with 15 minutes of time, 1.72 MPa of pressure and a moderate range of temperature (325°C to 345°C) can be used to achieve an excellent consolidation quality for high performance application of the Carbon/PEKK prepreg tape based thermoplastic composite material.

The outcome of this investigation is a contribution to the research database on thermoplastic composites, especially for the applications utilizing PEKK based composites.

5.3 Recommendations for future work

The thesis can be further extended on the following topics, which will constitute the future research work.

- A model can be developed to understand the flow behavior and matrix solidification under different processing conditions and to establish the mathematical relationship between those parameters and final properties.
- Simulation of the processing parameters for the fiber placement technology to fabricate a helicopter landing gear cross tube can be performed.
- Effect of processing parameters on the PEKK matrix characteristics such as crystallization kinetics, fiber matrix interaction and matrix degradation can be conducted.
- Annealing can be performed on laminates to investigate the difference in percent crystallinity and the corresponding consequences on mechanical properties.
- Variation in crystallinity of laminates because of specific cooling rates and their relation can be investigated.
- Further mechanical testing can be carried out on flexural, impact and delamination behavior of the laminates.
- More investigations can be performed to predict the effects of temperatures especially at a range which is at an extreme end of processing temperatures.

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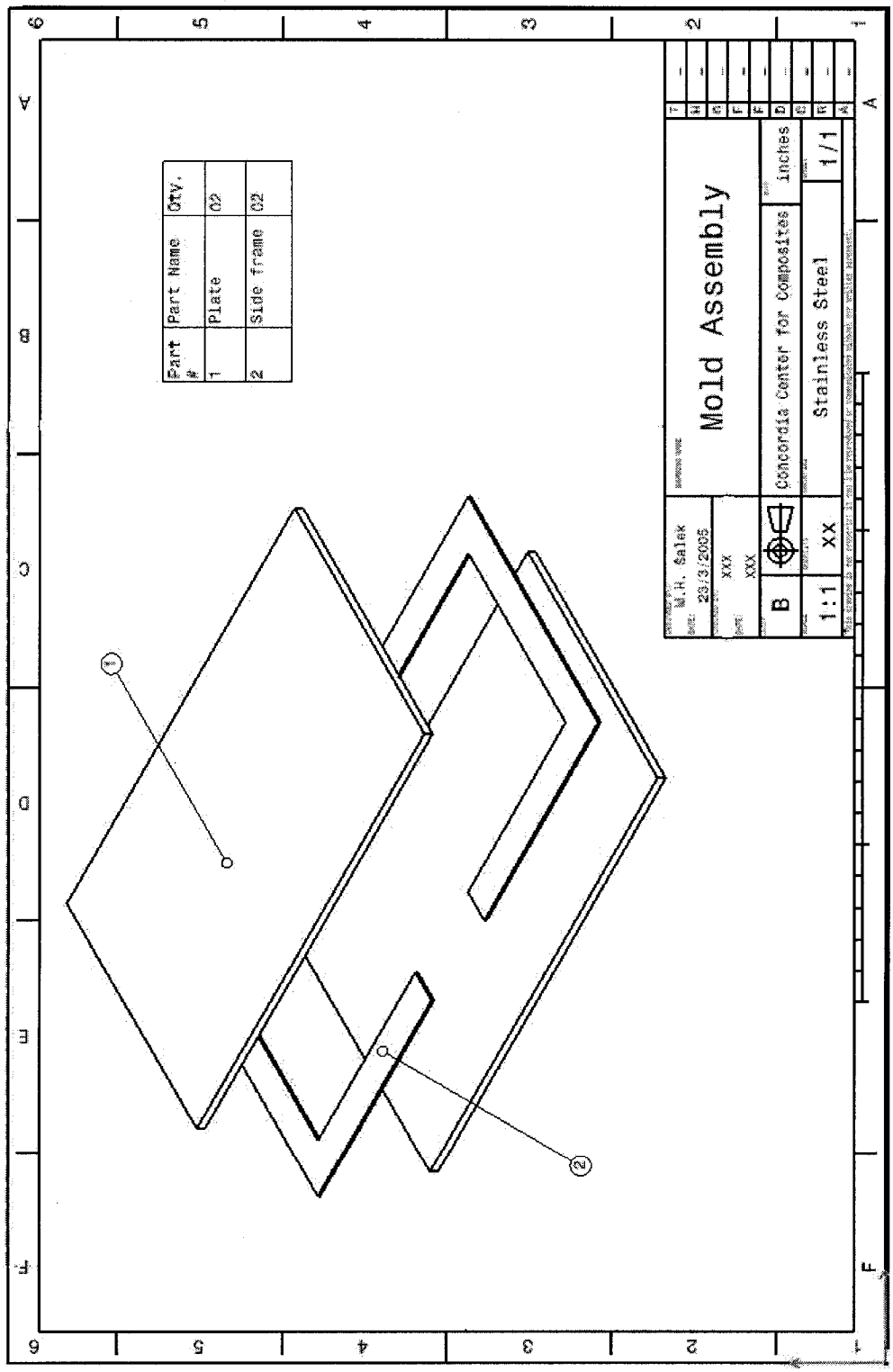
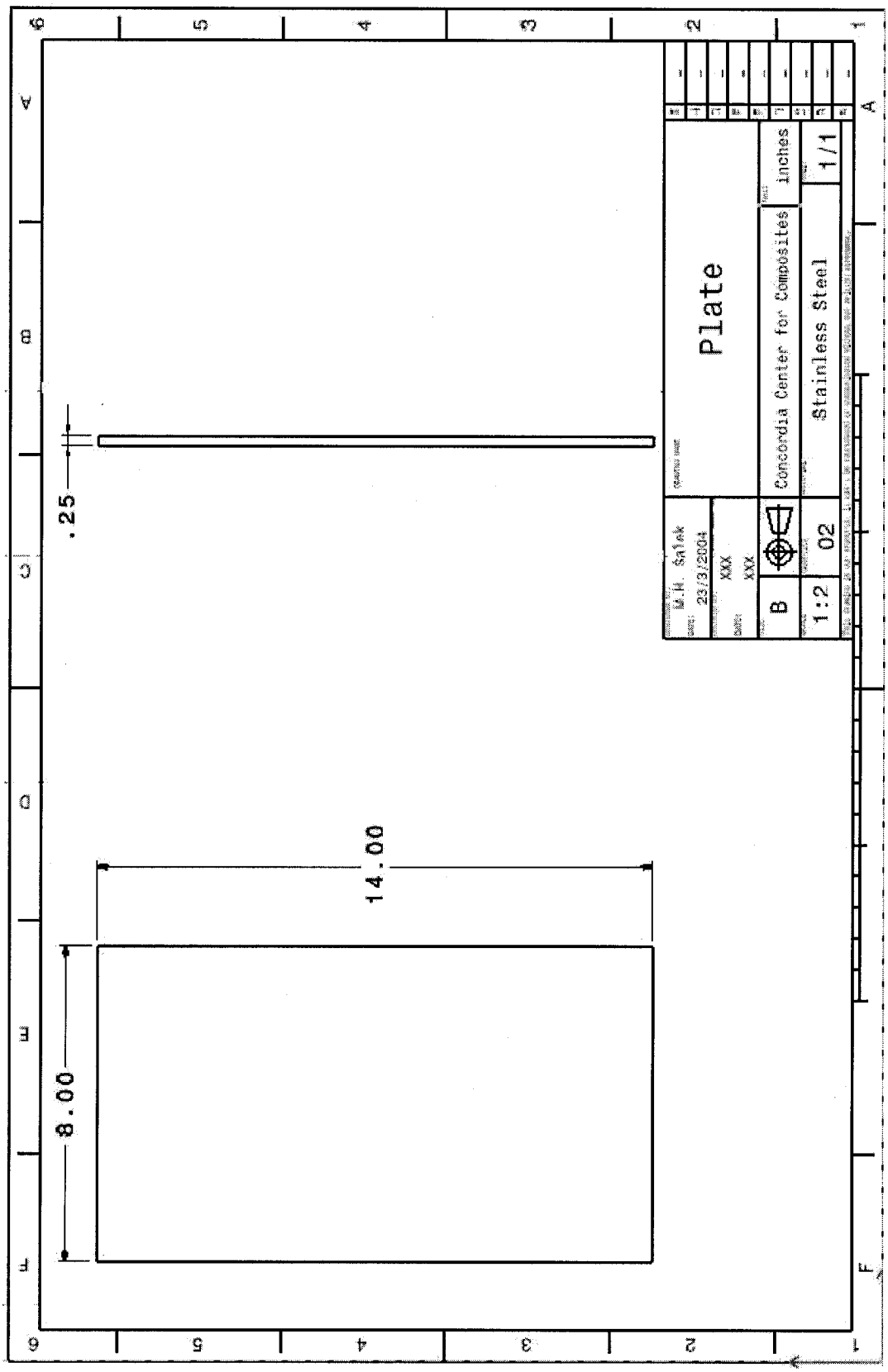
APPENDIX - A

Detail part and assembly drawing of the Steel Frame Mold.

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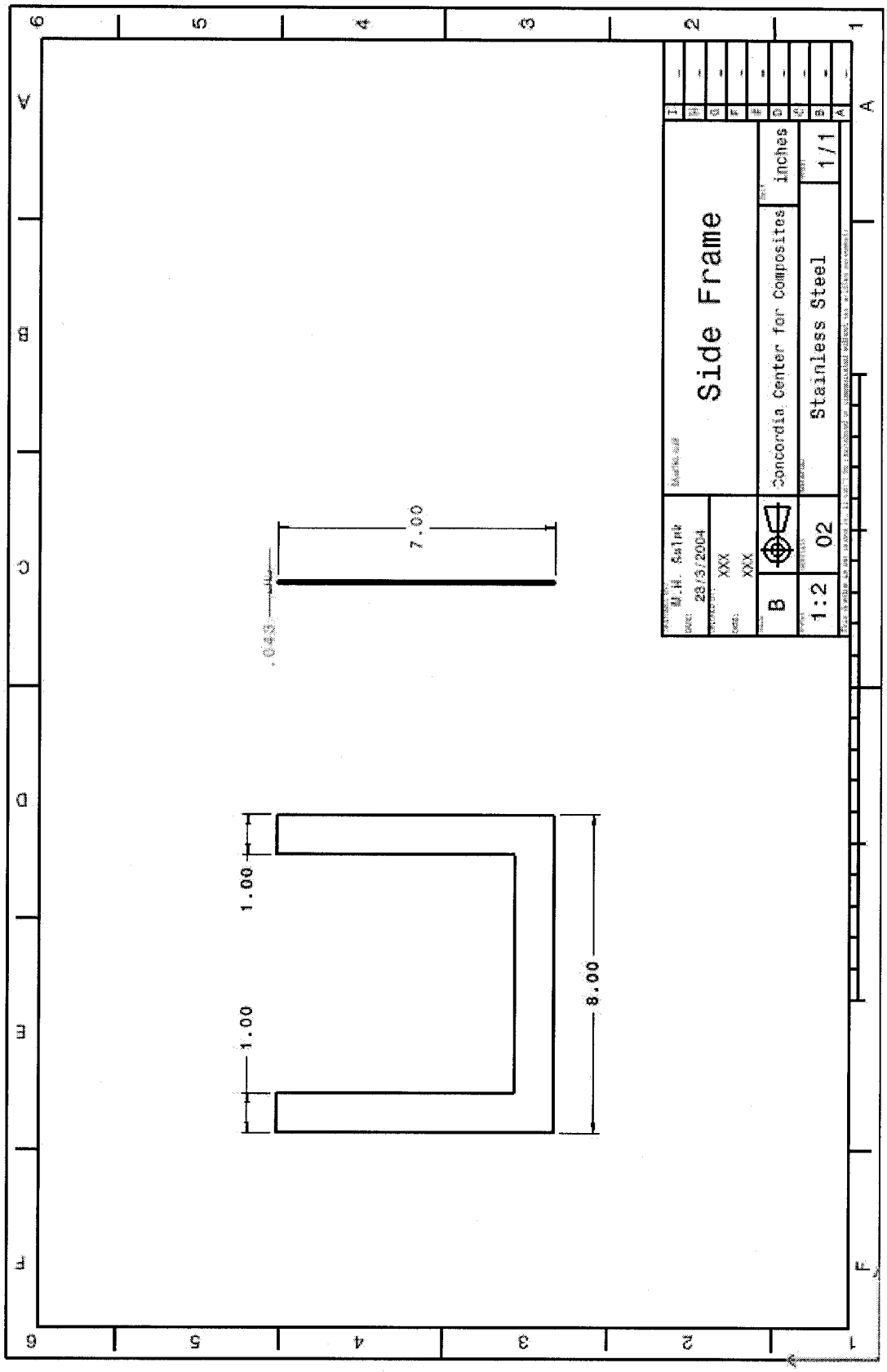
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